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RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES.[1]

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Introduction.

The purpose of the following research, as originally begun, was to study exhaustively the composition of natural gas as found in Western Pennsylvania. During a series of analyses by Bunsen's methods, using eudiometers calibrated with great care, and making readings by means of a Grunot cathetometer of superior construction, many difficulties were encountered which were not easily overcome. More exact methods for the positive identification of the various constituents of a gas-mixture seemed necessary, and finally a study of the qualitative reactions of gases was undertaken. Since the publication of Bunsen's *Gasometrische Methoden*, the introduction of the various forms of apparatus proposed by Hempel and Winkler has tended greatly to simplify quantitative gas-analysis.

The majority of absorption gasometric methods are based upon the assumption that the contraction undergone by the volume of a gas on exposure to a liquid reagent is not only a measure of the percentage of a particular constituent of the gas-mixture, but that the identity of such constituent is established by the same opera-

[1] Dissertation for the degree of Doctor of Philosophy, University of Pennsylvania. Read before The American Philosophical Society, March 17, 1893. Communicated by the author.

tion. This assumption is very often warranted by the facts, but occasionally leads to error. Qualitative methods, for the recognition of different gases, have usually been held wholly subordinate to quantitative absorption or explosion methods. Quantitative analyses are far more reliable if the constituents to be determined can be positively identified by independent methods; and it is somewhat strange that, heretofore, the qualitative side of gas-analysis should have received so small a share of attention. In the following work, an attempt has been made to collect together the more important reactions of the commonly occurring gases. The results must be regarded as a first attempt only, inasmuch as improved methods of preparation and purification will doubtless involve the necessity of corrections in certain cases. Accurate methods of qualitative gas-analysis are likely to prove of increasing importance in the study of the atmosphere, in the laboratory, and in the chemical arts. The following subdivision of the subject has been found convenient:

1. Phenomena of oxidation of hydrogen and hydrocarbons by air in presence of finely divided metals, and other oxidizing agents.

2. Reactions of gases towards various metallic salts and other compounds used in solution, and in a dry state at high temperatures.

I.—Phenomena of Oxidation of Hydrogen, Carbon Monoxide, Gaseous Paraffins, Olefines, and Acetylene.

Preparation of Palladium Asbestos.—Long-fibred asbestos, washed by hydrochloric acid, dried and weighed, was moistened with palladium-chloride solution. Alcohol was dropped on the asbestos and ignited. After burning off the alcohol a few times, the asbestos was heated in a Bunsen-burner flame, and the treatment with palladium chloride and alcohol repeated. With care, it is possible to obtain a fairly uniform coating of palladium, although the metal tends somewhat to collect on the surface of the fibers. Asbestos fiber, containing an amount of palladium equal to 6 per cent. of the total asbestos plus palladium, was used in the following experiments:

About 0.3 gram of this asbestos was placed in a glass tube of ½-inch bore. This tube was then heated in an iron oven, having its lower portion filled up to the level of the glass tube with iron

turnings, so that the glass tube rested on and was partly covered by the turnings. A thermometer was inserted into the turnings. In some of the experiments the apparatus described on page 168 was used. Two articles by W. Hempel[1] have appeared on the determination of hydrogen in gas-mixtures by means of palladium sponge. In the former article it is proposed to remove the hydrogen by occlusion; in the latter, by oxidation. Winkler[2] employs palladium asbestos for oxidation and determination of hydrogen in presence of methane (and other paraffins), in water-gas, coal-gas, etc. In order to study the limits and possibilities of these methods, and their applicability to various gas-mixtures, the following experiments were made:

1. *Hydrogen.*—Hydrogen is not easily obtained pure; all authors who have had occasion to study its properties agree upon this. The purest zinc contains carbon, and hydrogen made by the action of sulphuric acid upon this metal is contaminated by traces of hydrocarbons. Other metals have been tried. Aluminium was dissolved in sulphuric acid and also in caustic soda solution; magnesium and cadmium were dissolved in hydrochloric acid; sodium and potassium in water. In every case, however, the hydrogen evolved contains hydrocarbons, as was shown by the production of carbon dioxide on burning. After various trials, the following plan has been found to give satisfactory results: The purest zinc obtainable (such as is sold in sticks for use in Marsh's test for arsenic) was dissolved in dilute sulphuric acid. The gas was passed (1) through a 6-per cent. solution of permanganate of potassium acidulated by sulphuric acid; (2) through a glass tube containing cotton coated with precipitated oxide of copper;[3] (3) through alkaline permanganate; (4) the gas was kept in contact with bromine-water for twenty-four hours; (5) well washed by soda solution. I have found precipitated carbonate of copper in moist condition to answer better than the oxide, especially for removing sulphuretted hydrogen. Hydrogen so purified contained only traces of a paraffin which, calculated as methane, amounted to less than 0.02 per cent. of the hydrogen. By very careful tests, no phosphorus, arsenic, sulphur or antimony could be found.

[1] Ber. d. chem. Ges. **12**, 636, 1006 (1879).

[2] Technical Gas Analysis, p. 81.

[3] For the action of copper oxide as a purifying agent for hydrogen, see Lionet: Ztschr. anal. Chem. **19**, 344 (1880).

Experiment 1.—A mixture was made of hydrogen and air in the following proportions: air, 80; hydrogen, 20. This mixture, contained in a gas-holder, was caused to flow slowly over 6-per cent. palladium asbestos, which was contained in an ⅛-inch glass tube heated in the oven. The rate of flow of the hydrogen and air mixture could be controlled by causing it to bubble through sulphuric acid before entering the palladium-asbestos tube. Some anhydrous copper sulphate was placed in the far end of the palladium tube, which by its change of color to a bright blue serves as a delicate moisture-indicator. The rate of flow of the gas was 100 cc. in five minutes.

Temperature of Asbestos Tube.	Result.
20°	No moisture.
30	" "
40	" "
50	Moisture formed.
20	No moisture.
30	" "
40	" "
50	" "
55	Moisture formed.

Hence, absolutely dry hydrogen is not easily burnt by palladium asbestos below a temperature of 50°–60°.

At the above rate (100 cc. in five minutes) there is a strong tendency to cause glowing of the palladium asbestos, not throughout, but in minute points where the palladium had accumulated in thicker particles. This glowing may take place while the tube is at any temperature between 15° and 100°, and depends wholly on the rate of flow of the hydrogen mixture. It is independent of the temperature outside the tube, and it is therefore not possible to prevent or arrest it except by reducing the rate of flow. The hydrogen by its rate of burning determines the temperature, and the low specific heat of the palladium and feeble conductivity of the asbestos necessarily increase the tendency to glow. Using air and hydrogen (5 : 1) repeatedly, no explosion ever occurred, although the palladium often glowed with great intensity. This is also true of palladium asbestos containing 30 per cent. of palladium, and when the temperature was carried to 135° C. Air containing only 1 per cent. of hydrogen may cause intense glow-

ing of the palladium if the rate of flow is rapid. Immersion of the tube in cold water will not prevent glowing. Caution is necessary, should a mixture of oxygen and hydrogen be exposed to palladium. In experiments made with tubes of 1 mm. bore, and at a temperature of 100°, it was found that the hydrogen in burning causes a series of sharp explosions, very different from the quiet and slow oxidation which invariably characterizes the mixture of air and hydrogen.

Experiment 2.—To determine the degree of completeness of the oxidation of hydrogen by palladium asbestos. The mixture consisted of—air, 90; hydrogen, 10. The palladium tube was heated to 60°–70° C. Gas escaping from the palladium tube was passed through oil of vitriol and phosphoric anhydride, in order to dry thoroughly; then through a second (porcelain) tube containing palladium asbestos, and finally into a small weighed tube of phosphoric anhydride. The second palladium tube was heated to intense redness. It was found that absolutely no moisture was formed in the second contact with palladium, although 5 liters of the gas-mixture were used and the rate of flow varied from 40 to 100 bubbles per minute. It was shown, moreover, that complete oxidation is independent of the glowing of the palladium.

Hence the oxidation of hydrogen by air in presence of palladium is complete at a temperature of 60°–70° when the gas-mixture is dry. Quantitative experiments, to be detailed later, showed that in the case of air containing 0.2 per cent. of hydrogen a correct determination of the hydrogen was possible. The temperature in this case was 100° C. If the hydrogen and air mixture is moist, oxidation is easily and completely attained at ordinary temperatures.

Hydrogen is said to ignite at a temperature of 552° C.[1]

Experiment 3. *Gold Asbestos.* Air, 90; hydrogen, 10.—No change occurred till the gold asbestos was strongly heated over the flame, and even then the oxidation was exceedingly slow, so that repeated passages of the gas were required to produce complete oxidation. In the preceding experiment a Hempel's apparatus was used.

Experiment 4. *Platinum Asbestos.* Air, 90; hydrogen, 10.—The results were scarcely distinguishable from those obtained with palladium asbestos. Palladium causes oxidation with some-

[1] Le Chatelier: Bull. Soc. chim. (Paris) **39**, 2 (1883).

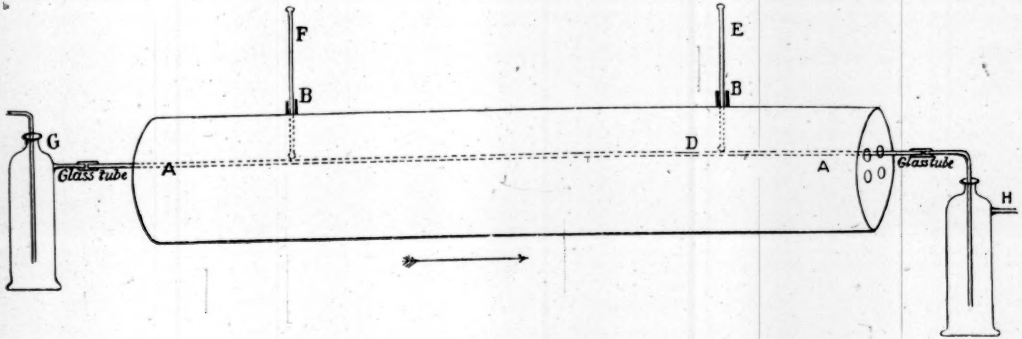
what greater intensity and at lower temperatures. Determinations of hydrogen in mixtures of known proportions, using a Hempel apparatus, gave very correct results.

Experiment 5. *Iridium Asbestos.* Air, 90; hydrogen, 10.—When used in a Hempel apparatus in the cold or at 100° C., iridium seemed to have very little influence, causing only a slight contraction in volume, even after the gas had passed the iridium many times.

Experiment 6. Air, 90; hydrogen, 10.—Palladium asbestos was moistened with a solution of carbonate of potash and dried at a heat which was insufficient to cause fusion or sintering. In several trials the alkali was found seriously to retard oxidation of the hydrogen, which was not fully burnt until the gas-mixture had been repeatedly (in one case ten times) passed through the tube at 100°.

Hydrocarbons.

Description of Apparatus.—A, is an iron gas-pipe, six inches in diameter and thirty-four inches long, closed at both ends by heavy asbestos board. Four iron pipes of $\frac{3}{16}$-inch bore are placed in the center, passing through the asbestos ends, and giving the apparatus the appearance of a boiler with four flues. *B*, *B*, are two side-necks of $\frac{1}{2}$-inch pipe. The whole interior space around the four small iron pipes is filled with iron turnings. Glass tubes of $\frac{1}{8}$-inch bore, containing the metal-coated asbestos or other reagent, could be pushed through the small iron pipes. Thermometers were placed in the side-necks *B*, *B*. Supposing the arrow to represent the direction of flow of the gas current through the gas-tubes, the metal-coated asbestos was, in the experiments, placed at the point *D*, and of the two thermometers *E* was kept a few degrees higher than *F*, the purpose being to have the gas heated nearly to the temperature of the hottest part of the oven before it reached that point. Thus it was not possible for the gas stream to exert a cooling effect upon the metal-coated asbestos. This apparatus is superior to an ordinary sheet-iron oven, as the glass tubes are heated by actual contact rather than by radiation. Repeated trials have shown that if a thermometer be inserted in the side-neck, and a second one in one of the long, horizontal iron tubes, the difference in the indications of the two thermometers will amount only to an insignificant fraction of a degree



IRON OVEN USED IN EXPERIMENTS UPON OXIDATION-TEMPERATURES.

Centigrade. Nitrogen-filled mercury thermometers were used up to 300° in the following experiments, and in order to measure higher temperatures, metallic salts of known fusing-point were employed. A few grains or crystals of the carefully purified salt were placed in a fine glass tube previously drawn out to a point. Such a tube was placed in the side-neck of the iron oven and plunged into the iron turnings. The temperature of oxidation of the hydrocarbon gas could then be ascertained to occur between the melting-points of two salts. This method, which is simply an adaptation of the process commonly used for the determination of melting-points, proved very satisfactory. It was not possible to employ an air-thermometer, as this would have necessitated an inconveniently large oven. The following list of substances, with their melting-points,[1] includes those which were used in the experiments detailed below:

Potassium nitrate	339°	Thallium iodide	439°
Potassium chlorate	359	Silver chloride	451
Lead iodide	383	Lead chloride	498
Cadmium iodide	404	Potassium iodate	582
Barium chlorate	414	Barium nitrate	593
Silver bromide	427		

The following general method was used in studying oxidation-temperatures of hydrocarbons:

Air containing a small measured percentage of the hydrocarbon was agitated with caustic soda solution to remove carbon dioxide. It was then caused to flow through the bottle *G* containing lime-water. This served to show whether the gas had been completely freed from carbon dioxide. The gas then traversed the palladium asbestos, or other reagent contained in the glass tube in the oven, and finally a second bottle of lime-water *H*. On heating the oven, the temperature of oxidation of the hydrocarbon could be recognized by the precipitate of carbonate of lime in the second lime-water bottle. As indicators for carbon dioxide in the oxidation-experiments, solutions of baryta, strontia and lime were all tried. The solubilities of the carbonates, according to Fresenius, are as follows:

$BaCO_3$	one part in	14,137	parts water.			
$SrCO_3$	"	"	"	18,045	"	"
$CaCO_3$	"	"	"	10,601	"	"

[1] Landolt and Börnstein's Tables, and J. Chem. Soc. **53**, 63 (1888).

Baryta-water appears to be the most delicate test. On account of its extreme sensitiveness, however, it is not easily preserved free from turbidity, and lime-water was found sufficiently sensitive for almost all purposes. The same general method above detailed was used in all the following experiments.

It seemed desirable at the outset to test the question, Do the hydrogen and carbon of a hydrocarbon burn simultaneously?

In the oxidation of a hydrocarbon in presence of excess of air, it seems probable that the hydrogen and carbon must burn simultaneously to water and carbon dioxide. It is possible, however, that under the conditions above described a selective oxidation of hydrogen might occur, involving the formation of a condensation-product. Thus methane might yield acetylene and no carbon dioxide, $2CH_4 + O_3 = 3H_2O + C_2H_2$; or methane might yield ethylene and no carbon dioxide, $2CH_4 + 2O = C_2H_4 + 2H_2O$.

As reagents for the detection of moisture in a gas, the following substances were tried: anhydrous cobalt chloride, anhydrous copper sulphate, phosphoric anhydride, a mixture of green vitriol with ferricyanide of potassium, the green vitriol being in its crystallized form, $FeSO_4.7H_2O$.[1] This salt and the ferricyanide of potassium were ground separately and mixed just previous to the experiment. A little of the mixture placed in the end of the glass tube was found to be a delicate indicator for moisture, assuming quickly a deep blue color.

Experiment 7. Air, 96.9; ethylene, 3.1 —This gas-mixture was passed through soda solution and then dried by oil of vitriol. It then traversed the palladium asbestos, which was gradually heated in the oven. At the far end of the same glass tube the gas passed over about 0.1 gram of the green vitriol and ferricyanide of potassium mixture (cold), and finally into lime-water. It was found that the lime-water became milky a few moments before the powder turned blue. This change to blue took place, however, immediately afterwards and before any further increase in the temperature of the oven had occurred. As the lime-water is a much more sensitive reagent towards carbon dioxide than is the green-vitriol mixture towards moisture, it is natural that the carbon dioxide should produce its effect a little in advance of the water-vapor. Similar experiments were tried with methane. The results were the same as with ethylene.

[1] Anhydrous sulphate of iron was found not to give satisfactory results.

Experiment 8. Air, 96.9; methane, 3.1.—This mixture (moist) was found, after passing the palladium asbestos, to cause no reduction in palladium-chloride solution (see reactions in solution), and hence no oxidation of methane to ethylene had occurred. There is therefore no reason to suppose that, under the circumstances which prevailed in the apparatus above described, either constituent of the hydrocarbon is oxidized before the other. The hydrocarbon yields directly carbon dioxide and water.

Paraffins.

2. *Methane.*—This hydrocarbon was prepared by the method of Gladstone and Tribe.[1] Methyl iodide of normal boiling-point was caused to flow in admixture with alcohol upon "copper-zinc couple." The resulting gas was freed from alcohol-vapor by oil of vitriol. It was then washed with bromine-water, and the bromine-vapors subsequently removed by ferrous sulphate solution. Finally it was passed over dry palladium chloride at 50°, to remove any possible traces of hydrogen. The following explanation of the reaction is given by the authors cited:

$$CH_3I + Zn(Cu) + H_2O = CH_4 + Zn\langle^{I}_{OH} + Cu.$$

200 cc. of the methane so prepared were burned, and the products aspirated through soda solution. On testing the latter for halogen, no traces could be found. From this it was evident that no vapor of methyl iodide had escaped decomposition by the zinc. Methane is obtained when chloroform dissolved in alcohol is dropped upon zinc powder:[2]

$$CH_3Cl + 3H_2O + 6Zn = 3ZnO + 3ZnCl_2 + 2CH_4.$$

This method was found to give very satisfactory results. The process usually given in the text-books, by heating acetate of soda with alkali, is very unsatisfactory both as regards the purity and the quantity of product.

Experiment 9. *Palladium Asbestos.* Air, 96.9; methane, 3.1.—Oxidation to carbon dioxide occurred at the following temperatures: (1), (2), and (4), above melting-point of cadmium iodide (404°); (3) and (5), above melting-point of barium chlorate (414°).

[1] J. Chem. Soc. **45**, 154 (1884). [2] Sabanejeff: Ber. d. chem. Ges. **9**, 1810 (1876).

In the above trials methane from methyl iodide was used.

The preceding experiment was repeated, using methane and chloroform. In six different trials the temperature of oxidation was found to be between the melting-points of cadmium iodide and silver chloride (404° and 451°). In one trial, oxidation occurred considerably above the melting-point of silver chloride. The temperature of oxidation of methane is therefore extremely high as compared with that of hydrogen.

Hempel, in his excellent work on gas analysis, says that methane prepared from sodium acetate is oxidized by palladium at 210°. My results do not confirm this statement. The difference is possibly due to impurities in the methane.

Experiment 10. *Palladium-Platinum Asbestos.* Air, 96.9; methane, 3.1.—Asbestos was moistened alternately with palladium chloride and platinum chloride and the metals reduced by burning alcohol, as already described, the object being to produce an intimate mixture of both in finely divided state. Oxidation occurred in four trials between the melting-points of cadmium iodide and silver chloride. The mixture of the two metals is, therefore, no more efficient than palladium alone.

Experiment 11. *Platinum Asbestos.* Air, 96.9; methane, 3.1. —Oxidation occurred in five trials at a temperature just below the melting-point of silver chloride.

Experiment 12. *Gold Asbestos.* Air, 96.9; methane, 3.1.— Oxidation occurred at a temperature of dull redness. In this last experiment a Hempel apparatus was used.

According to Mallard and Le Chatelier,[1] methane inflames at 780°.

3. *Ethane.*—This gas was prepared from ethyl iodide by the method of Gladstone and Tribe already described. The resulting gas was purified from alcohol-vapors by prolonged contact with oil of vitriol. It was then treated with potash solution and with palladium chloride (dry). 200 cc. of the gas so purified yielded, on burning, no trace of halogen when the product of combustion was aspirated through potash solution.

Experiment 13. *Palladium Asbestos.* Air, 96.1; ethane, 3.1. —In several trials made with ethane, the temperature of oxidation was found to be between the melting-points of cadmium iodide and silver chloride. Parallel trials were then made, using

[1] Ann. des Mines, 1880, p. 201.

air containing 3.1 per cent. of methane (from methyl iodide) in one tube and 3.1 per cent. ethane in the other. Both tubes were charged with portions of the same lot of palladium asbestos, and both were heated simultaneously in the iron oven, so that the conditions to which the two gases were subjected were as nearly as possible identical. In ten trials oxidation occurred in both tubes in the neighborhood of the melting-point of silver chloride; but it was noticeable that the methane was oxidized in eight of the experiments a little earlier (and hence at a slightly lower temperature) than the ethane. The more complex hydrocarbon ethane is at least as stable, and probably somewhat more stable, than the lower methane. A parallel case is probably to be found in the difference in stability of the corresponding alcohols towards reducing agents. Methyl alcohol is decomposed on warming with powdered zinc, with formation of carbon monoxide and hydrogen, while ethyl alcohol is unaltered except at a red heat.[1]

4. *Propane.*—This hydrocarbon was prepared by Gladstone and Tribe's method, from isopropyl iodide and "copper-zinc couple." The reaction is much slower than in the case of methane and ethane; the yield is, however, satisfactory. The same method of purification was used as in the case of methane. The gas was found to be free from iodine compounds.

Experiment 14. *Palladium Asbestos.* Air, 96.9; propane, 3.1. —Oxidation occurred at the following temperatures: (1) and (3), above melting-point of potassium nitrate (339°); (2), just below melting-point of potassium nitrate (339°); (4), just below melting-point of lead iodide (383°); (5) and (6), at melting-point of potassium chlorate (359°).

5. *Isobutane.*—This hydrocarbon was prepared by the method of Gladstone and Tribe from isobutyl iodide and "copper-zinc couple." It was purified by the method followed in the case of the preceding hydrocarbon, and was proved to be free from iodine compounds.

Experiment 15. *Palladium Asbestos.* Air, 96.9; isobutane, 3.1—Oxidation occurred at the following temperatures: (1), 236°; (2), 225°; (3), 250°; (4), 220°; (5), 225°; (6), 250°.

Experiment 16.—The same mixture of air and isobutane was conducted over ruthenium asbestos (prepared by the use of ruthenium chloride in the same manner as the palladium asbestos

[1] Jahn: Grundsätze der Thermochemie, p. 150.

already described). Oxidation occurred at the following temperatures: (1), 250°; (2), 236°; (3), 230°; (4), 225°; (5), 222°; (6) 214°.

As regards this more easily oxidizable hydrocarbon, ruthenium and palladium have almost the same action.

6. *Pentane.*—Petroleum gasolene, which had been kept several weeks in contact with concentrated sulphuric acid, was fractionated and the fraction boiling at about 37° C. was used for the following experiments. It was mainly pentane, as was shown by a vapor-density determination, but contained, no doubt, small quantities of other low-boiling paraffins. Pure air was aspirated through a Woulfe bottle containing a little of the liquid.

Experiment 17. *Palladium Asbestos.*—Oxidation occurred at (1), 210°; (2), 200°; (3), 180°; (4), 170°; (5), 210°.

7. *Heptane.*—"Theoline," a commercial product formerly replacing benzene in the San Francisco market, and manufactured by distilling a resin from the tree *Pinus sabiniana*, was shown by Thorpe[1] to consist of normal heptane in an impure state. By digestion with oil of vitriol the paraffin is obtained pure and of constant boiling-point (between 98° and 99° C.). Heptane was the highest paraffin used in the trials of oxidation-temperatures. As this hydrocarbon is readily obtained in a state of purity, and as it was the most complex paraffin employed, it seemed desirable to ascertain whether, on oxidation by palladium asbestos, any unsaturated hydrocarbon resulted.

Experiment 18. *Palladium Asbestos.*—Air was aspirated through a Woulfe bottle containing heptane and then through the heated palladium-asbestos tube. Oxidation occurred at the following temperatures: (1), 270°; (2), 270°; (3), 280°; (4), 275°; (5), 300°; (6), 290°.

While the experiment was in progress, the air escaping from the palladium-asbestos tube was passed through soda solution to absorb the carbon dioxide formed, and then into palladium-chloride solution and finally into lime-water. The palladium chloride was reduced to metal and the lime-water following it was rendered milky (see reaction of carbon monoxide in solution). This result occurred only when the air was insufficient for complete oxidation of the heptane. With an excess of air, only carbon dioxide and water were formed, and no unsaturated hydrocarbon

[1] J. Chem. Soc. **35**, 296 (1879).

could be detected (olefines and acetylenes would have caused a reaction in palladium-chloride solution; see reactions of these hydrocarbons in solution). It seems, therefore, that oxidation of the paraffins CH_4, C_2H_6 . . . C_7H_{16} (even when carried on at the lowest possible temperatures) by excess of air in presence of palladium asbestos yields only carbon dioxide and water, although by no means in quantities proportional to the amount of the hydrocarbon originally used.

Olefines.

8. *Ethylene.*—This hydrocarbon, on account of the ease with which it is prepared and its low temperature of oxidation, is well suited to the study of reactions, and it has received in the present work a larger share of attention than any other gas.

Ethylene was prepared by the method of Erlenmeyer and Bunte.[1] The yield is, however, small as compared with the theoretical. The older method of Mitscherlich,[2] according to which the vapor of boiling alcohol is led into a mixture of 10 parts sulphuric acid and 3 parts water, at a temperature of 165° C., yields more ether than ethylene, although it possesses the advantage that frothing is avoided. Whatever the strength of the sulphuric acid used, there is always produced a large proportion of ether which cannot be absorbed by rapid bubbling through sulphuric acid. Part of this ether-vapor is removable by agitation with a large volume of cold water. Its complete removal requires prolonged contact with oil of vitriol. The gas was purified by soda solution containing bichromate of potash and digested with oil of vitriol for several days.

Ethylene was also prepared by the action of zinc upon ethylene dibromide.[3] Ethylene dibromide dissolved in 2 parts alcohol was introduced by tap-funnel into a flask containing zinc powder, and connected by a reversed condenser with a gasometer. The same method of purification by sulphuric acid was used as in the preceding case. This method is in every way very satisfactory for the preparation of small quantities of ethylene.

Experiment 19. *Palladium Asbestos.* Air, 96.9; ethylene, 3.1. —Oxidation occurred at (1), 210°; (2), 180°; (3), 224°; (4), 200°; (5), 220°; (6), 191°; (7), 224°.

[1] Ann. Chem. (Liebig) **168**, 64 (1873). [2] Kolbe: Lehrb. d. organ. Chem., Vol. I, p. 349.
[3] J. Chem. Soc. **27**, 406 (1874).

The ethylene burns therefore more easily than either methane or ethane.

Experiment 20. *Palladium-Platinum Asbestos.*—The same mixture of ethylene and air was used. The range of temperatures at which oxidation occurred was about the same as in the case of the preceding experiment, showing that the mixture of the two metals is no more efficient than palladium alone.

Experiment 21. Air, 96.9; ethylene, 3.1.—30-per cent. palladium asbestos was moistened with cobalt-nitrate solution, dried and ignited in order to coat the asbestos with peroxide of cobalt. On passing the gas-mixture, carbon dioxide was produced at the following temperatures: (1), 277°; (2), 250°; (3), 260°. Hence the presence of an easily reducible metallic oxide does not seem to increase the oxidizing action of the palladium.

Experiment 22.—Several trials were then made in order to ascertain whether by the same general method ethylene could be exhaustively burned. It was found that, using air containing 3.1 per cent. of ethylene, oxidation is complete (*i. e.* to carbon dioxide and water) only when the palladium asbestos is brought to a temperature of bright redness. At a dull red heat the hydrocarbon may pass partially unburnt. A platinum wire spiral (heated by an electric current) was found to be less efficient than palladium asbestos.

Experiment 23. *Absorption of Ethylene by Palladium.*—Pure ethylene (*i. e.* unmixed with air) was passed over 2 grams of finely divided palladium contained in a Hempel tube heated to 100°. A considerable absorption of the gas occurred, varying in several trials from 0.5 to 5 cc., according to the duration of the experiment. Unmixed with an excess of air, it appears, therefore, that ethylene may undergo an absorption which might cause serious errors in a quantitative gas-analysis. With palladium asbestos (6 per cent. palladium) no occlusion of ethylene sufficient to affect the volume of the gas could be observed.

Experiment 24. *Ruthenium Asbestos.* Air, 96.9; ethylene, 3.1.—Oxidation occurred at the following temperatures: (1), 294°; (2), 281°; (3), 274°; (4), 320°.

Experiment 25. *Osmium Asbestos.* Air, 96.9; ethylene, 3.1.—Owing to the volatility of osmium in the form of oxide, some difficulty was found in preparing osmium asbestos. Osmic acid was reduced by alcohol and the reduced metal spread upon asbestos.

Oxidation occurred at the following temperatures: (1), 150°; (2), 140°; (3), 135°; (4), 120°; (5), 116°; (6), 160°; (7), 170°; (8), 160°; (9), 160°; (10), 135°.

In the preceding experiments it has been shown that oxidation of the hydrocarbon does not occur each time at the same temperature. The variations are often so great as to preclude the supposition that a cause is to be sought in different conditions of the experiment. To ascertain as fully as possible the limits of variation in the temperature of oxidation the following trials were made:

Experiment 26.—Instead of metal-coated asbestos, a platinum wire 1 mm. thick and 1 inch long was placed in the $\frac{1}{8}$-inch glass tube in the oven. The same mixture of air and ethylene was used as in the preceding experiments. As in all previous work, the oven was allowed to cool down after each trial and before the next one was begun. In every case the temperature was very gradually raised until oxidation, as indicated by the precipitation in the lime-water, occurred. The gas stream was carefully regulated, being maintained at a uniform rate in all the trials. Oxidation occurred at the following temperatures: (1), 270°; (2), 290°; (3), 390°; (4), 290°; (5), 310°; (6), 289°; (7), 295°; (8), 300°; (9), 300°; (10), 265°; (11), 210°; (12), 217°; (13), 220°; (14), 225°; (15), 200°; (16), 210°; (17), 220°; (18), 255°; (19), 210°; (20), 220°; (21), 235°; (22), 200°; (23), 210°; (24), 225°.

As no effort had been spared to secure absolute uniformity of conditions, the conclusion seems justified that oxidation of the hydrocarbon ethylene occurs within somewhat wide limits of temperature.

Experiment 27.—Air containing 3.1 per cent. ethylene was passed through a glass tube containing pieces of glass tubing which had been previously ignited. During four hours no oxidation occurred at the melting-point of bromide of silver (427°).

Experiment 28. Air, 96.9; ethylene, 3.1.—This mixture was passed, as before, over a platinum wire and the temperature gradually raised until a carbon-dioxide reaction was produced. This occurred at 240°. The gas stream was then continued while the temperature was allowed to fall. The lime-water was repeatedly replaced, but each time became rapidly milky. Oxidation was continuous until the temperature fell to about 110°, at which point fresh lime-water was found to remain clear. Hence, platinum

having been sufficiently heated to induce oxidation of ethylene by atmospheric oxygen, retains this power while the temperature is lowered to a point which would have been wholly insufficient to cause such oxidation if the temperature were rising instead of falling. This is true, moreover, when the gas stream flows at the rate of 20 to 50 bubbles per minute; so slowly, therefore, that there is no possibility that this effect is attributable to an actual burning of the gas with flame. Similar results were obtained in trials with palladium asbestos and ruthenium asbestos, and also when methane and ethane were used.

9. *Propylene.*—This gas was prepared by the action of potash on propyl iodide.[1] 80 grams of propyl iodide were heated with 50 grams of potash and 50 grams of alcohol over the water-bath. The following reaction occurs:

$$C_3H_7I + KOH = KI + H_2O + C_3H_6.$$

The flask containing the potash and alcohol being connected with a reverse condenser and gently warmed, the propyl iodide is slowly added by a tap-funnel, and at a temperature of 40° the reaction begins. The gas so produced was washed with water and digested with oil of vitriol (cold) in which it is insoluble, and finally washed by potash solution. Propylene was also prepared from allyl iodide.[2] 20 cc. of allyl iodide mixed with three volumes of alcohol were poured over 30 grams powdered zinc containing 10 grams of mossy zinc heated in a flask over a water-bath. Powdered zinc becomes during the reaction a hard, compact mass. The addition of mossy zinc and constant agitation serve to facilitate the process. The reaction is as follows:

$$C_3H_5I + C_2H_5OH + Zn = Zn\begin{matrix}\nearrow OC_2H_5 \\ I\end{matrix} + C_3H_6.$$

The propylene so prepared was purified as in the preceding method. Careful tests demonstrated the absence of iodine compounds from the product. Beilstein and Wiegand[3] prepare propylene by the action of propyl alcohol upon phosphoric anhydride. In employing this method, 120 grams phosphoric anhydride were placed in a flask provided with a reversed condenser and propyl alcohol gradually added by a tap-funnel. The action is at

[1] Erlenmeyer: Ztschr. Chem. [1] **7**, 617 (1864).

[2] Gladstone and Tribe: J. Chem. Soc. **27**, 208 (1874); and also Niderist: Ann. Chem. (Liebig) **196**, 358 (1879).

[3] Ber. d. chem. Ges. **15**, 1498 (1882).

first very violent and requires cooling of the flask; becomes less and less intense, and finally it is found necessary to heat the flask over asbestos. After about 130 cc. of propyl alcohol had been added the reaction ceased. The method is satisfactory although the yield is small. A method proposed by Claus and Kerstein,[1] according to which zinc-dust is heated with glycerine, was tried, but with unsatisfactory results. The intense frothing of the mixture renders the process uncontrollable. In the various trials, propylene, as prepared by the first three methods just described, was used. That prepared from allyl iodide seemed to be the purest, as judged by the reactions in solution to be detailed later.

In the oxidation-experiments below cited, propylene from allyl iodide is understood to have been used.

Experiment 29. *Palladium Asbestos.* Air, 96.9; propylene, 3.1.—Oxidation occurred at (1), 170°; (2), 180°; (3), 200°; (4), 200°.

Experiment 30. *Ruthenium Asbestos.*—The same mixture of propylene and air was used. Oxidation occurred at (1), 235°; (2), 252°; (3), 256°; (4), 239°.

Experiment 31. *Rhodium Asbestos.*—The same mixture of air and propylene. Oxidation occurred at (1), 283°; (2), 284°; (3), 270°; (4), 290°.

10. *Trimethylene.*—This very interesting hydrocarbon was obtained from trimethylene dibromide by the action of metallic zinc.[2] 20 cc. trimethylene dibromide with 60 cc. of alcohol were poured over 60 grams of zinc dust. The reaction is as follows:

$$\begin{array}{l} CH_2Br \\ | \\ C:H_2 \\ | \\ CH_2Br \end{array} + Zn = \begin{array}{c} CH_2 \\ \diagup\diagdown \\ CH_2 - CH_2 \end{array} + ZnBr_2.$$

The trimethylene dibromide molecule, on losing bromine, assumes the form of a ring, and the resulting hydrocarbon is therefore a saturated compound. The gas is evolved at a gentle heat (the temperature should not exceed 60°), and is purified by passing through a condenser cooled by ice, by digestion with sulphuric acid and, finally, by dilute permanganate of potash solution. It has been shown by Wagner[3] that trimethylene pre-

[1] Ber. d. chem. Ges. **9**, 695 (1876).
[2] Gustavson: J. prakt. Chem. [2] **36**, 300 (1887); Ber. d. chem. Ges. (Ref.) **20**, 707 (1887).
[3] *Ibid.* **21**, 1230 (1888).

pared by the above reaction is liable to contain propylene, which may be removed by prolonged contact with a weak solution of permanganate of potash which converts propylene into its corresponding glycol, but does not attack the trimethylene.

Experiment 32. *Palladium Asbestos.* Air, 96.9; trimethylene, 3.1.—Oxidation occurred at (1), 260°; (2), 290°; (3), 270°.

Experiment 33. *Osmium Asbestos.*—The same mixture of air and trimethylene. Oxidation occurred at (1), 200°; (2), 200°; (3), 180°; (4), 165°.

This hydrocarbon seems to stand intermediate between propane and propylene as regards resistance to oxidation.

11. *Isobutylene.*—This hydrocarbon was prepared by the action of sulphuric acid upon isobutyl alcohol, by the method of Puchot.[1] 100 grams isobutyl alcohol were mixed (cold) with 100 grams oil of vitriol, 160 grams sulphate of calcium and 40 grams bisulphate of potassium. This mixture was heated, using a flask with reversed condenser, to a temperature sufficient to cause a rapid evolution of gas. Besides butyl ether and other less volatile compounds, impurities in vapor form resulting from this process occur in the isobutylene, which is on this account unsatisfactory. The yield is comparatively large.

By the action of potash upon isobutyl iodide a much purer product is obtained. Isobutyl bromide may be used instead of the iodide. In either case the use of potash in powdered form greatly facilitates the reaction. Potassium iodide, being more soluble in alcohol than potassium bromide, the alkyl iodide is to be preferred in reactions of the above type, as potassium bromide, resulting from the use of alkyl bromides, encrusts the potash and retards the reaction.

Isobutylene prepared by the latter method was used in the following experiments. It was carefully purified by digestion (cold) with sulphuric acid, and on testing was found to be free from iodine compounds. Isobutylene is soluble in water to a considerable extent and should therefore be collected over salt solution.

Experiment 34. *Palladium Asbestos.* Air, 96.9; isobutylene, 3.1.—Oxidation occurred at (1), 180°; (2), 160°; (3), 170°; (4), 185°; (5), 155°.

12. *Acetylene.*—100 grams crushed potash were placed in a flask connected with reversed condenser; a mixture of 50 grams

[1] Ann. chim. phys. [5] **28**, 508 (1883); Ber. d. chem. Ges. **16**, 2284 (1883).

ethylene bromide with 150 grams alcohol was added in small portions by a tap-funnel. The escaping acetylene was caused to bubble through boiling potash solution and then absorbed by ammoniacal cuprous-chloride solution. The resulting red precipitate was washed with ammoniacal copper solution, then by weak ammonia. After washing, the precipitate was brought into a flask and decomposed by hydrochloric acid, and the acetylene thus evolved was collected. The copper precipitate consists of the compound Cu_2C_2,[1] and on treatment with hydrochloric acid undergoes the reaction:

$$Cu_2C_2 + 2HCl = Cu_2Cl_2 + C_2H_2.$$

The precipitate of copper acetylide must be preserved in an unoxidized state previous to its treatment with hydrochloric acid in order to liberate acetylene. If exposed to air during washing, the precipitate is found to remain almost unacted upon by hydrochloric acid, and the yield of acetylene from the copper compound will be insignificant. On this account the washing should be conducted in an atmosphere of carbon dioxide.

A very interesting method for the preparation of acetylene by the action of water upon barium carbide has been described by Maquenne.[2] Barium carbonate is reduced by magnesium powder in presence of excess of carbon. As the result of the somewhat violent reaction barium carbide is formed. On moistening with water this carbide is decomposed, yielding nearly pure acetylene.

Experiment 35. *Palladium Asbestos.* Air, 96.9; acetylene, 3.1. —Oxidation occurred above melting-point of (1), potassium nitrate (339°); (2), potassium chlorate (359°); (3), potassium nitrate (339°); (4), potassium nitrate (339°).

It was found by careful tests that no carbon monoxide is formed in the case of the above mixture. In fact, no other products resulted than carbon dioxide and water.

Acetylene seems therefore to be more stable towards heated air in presence of palladium asbestos than the olefines, and in this respect even to rival the paraffins.

13. *Benzene.*—The low boiling-point of benzene and the common occurrence of its vapor in gas-mixtures justify its consideration in connection with the gaseous hydrocarbons.

[1] For an interesting description of this compound, see Keiser: This Journal **14**, 285 (1892).
[2] Compt. Rend. **115**, 558 (1892).

Experiment 36.—Air aspirated through benzene (prepared from benzoic acid) and then through palladium asbestos was found to yield carbon dioxide at the following temperatures: (1), 290°; (2), 250°; (3), 270°.

Benzene-vapor causes the palladium to glow very easily; in fact, much more readily than any of the hydrocarbons heretofore tried.

14. *Alcohol-Vapor. Experiment* 37.—Employing the same method detailed in the case of benzene, oxidation was found to occur at (1), 160°; (2), 240°; (3), 150°; (4), 150°.

15. *Xylenes.*—Very careful experiments with the vapors of meta-, para- and ortho-xylene were tried, as it seemed possible that these three isomers might exhibit different temperatures of oxidation dependent upon the position of the side-chain. No satisfactory results were obtained, however, on account of the want of constancy of these hydrocarbons as regards oxidation-temperature.

16. *Carbon Monoxide.*—This gas was prepared by the action of sulphuric acid upon oxalic acid. It was purified by caustic soda solution.

Experiment 38. *Palladium Asbestos.* Air, 90; carbon monoxide, 10.—Oxidation occurred at the following temperatures: (1) and (2), at the melting-point of potassium nitrate (339°); (3), at (290°); (4), at the melting-point of potassium nitrate; (5), above the melting-point of potassium nitrate; (6), at the melting-point of potassium chlorate (359°).

Trials were also made in varying the rate of flow, and also with different proportions of carbon monoxide and air. The results did not differ materially from those just cited. This gas seems to stand intermediate between methane and ethylene in its resistance to oxidation.

Experiment 39. *Ruthenium Asbestos.*—Using the same air mixture, oxidation occurred at the following temperatures: (1), 194°; (2), 209°; (3), 182°; (4), 188°.

The preceding experiments serve to illustrate some important facts regarding the oxidation of gaseous hydrocarbons.

1. The temperature of oxidation is mainly dependent upon the solid bodies with which the gas is in contact—a fact which is not new.

2. Two phases are often, but not always, to be observed in the process of oxidation. As the temperature rises, a point is reached at which a minute and scarcely recognizable trace of carbon dioxide appears. After the slow oxidation has continued for some time and gradually increased during a rise of temperature of 20, 30, or even more degrees, a sudden intense reaction occurs in the lime-water, suggesting the change from smouldering fire to actual flame. Very often this slow oxidation is not observed and the carbon dioxide reaction occurs in the lime-water suddenly and with full intensity. The hydrocarbon molecule seems to exist at high temperatures in a condition of unstable equilibrium towards oxygen. In the preceding statements the temperatures given are those of decided and intense reaction in the lime-water.

3. The oxidation of a hydrocarbon by air, under conditions similar in all respects, does not occur always at the same temperature. It may vary within rather wide limits of the thermometer scale. A variation in the proportion of hydrocarbon and air does not seem materially to influence the oxidation-temperature.

4. The paraffins are the most stable towards heated air in presence of palladium. Acetylene and carbonic oxide stand next in order. The olefines are the most easily oxidized.

5. Of the members of the same homologous series of hydrocarbons, the lower are the more stable towards oxidizing influences.

6. Hydrogen stands alone among combustible gases in undergoing oxidation under the influence of palladium-coated asbestos in the cold.

7. Oxidation of gaseous hydrocarbons in excess of air involves the simultaneous formation of carbon dioxide and water.

8. In all cases where air is in excess, oxidation is complete (*i. e.* yielding only carbon dioxide and water), even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, carbon dioxide may be partly replaced among the products of oxidation by carbon monoxide.

9. As regards oxidizing power, the metals which I have studied might be arranged in the following order, beginning with the most active: (1) Osmium, (2) palladium, (3) platinum, ruthenium, (4) iridium, (5) rhodium, (6) gold.

Osmium is decidedly the most powerful, causing oxidation of ethylene even below 150°. Rhodium is less efficient as regards oxidation of hydrogen than palladium. Oxidizing power is

apparently not dependent upon atomic weight. Of these metals, osmium in fine division is the most easily converted into an oxide. Heated in a flame it burns, exhibiting much the appearance of burning lampblack, and yields, as is well known, the volatile osmium tetroxide. At much lower temperatures the metal is slowly oxidized and volatilized. Palladium in fine division is converted into a stable oxide, Pd_2O, on heating to redness.[1] Platinum and gold are not oxidizable in air at any temperature. Ruthenium oxidizes to a sesquioxide at a red heat. Rhodium is convertible into a monoxide. In the case of the majority of these metals, the tendency to form an unstable oxide, which readily gives up its oxygen, explains the oxidizing power upon hydrocarbons. When it is considered, however, that platinum, which induces oxidation nearly as readily as palladium, does not produce directly an oxide when heated in air, the oxidizing power possessed in common by these metals seems to require further explanation.

10. At a bright red heat and in excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper.

11. Glowing of the palladium is by no means essential to slow oxidation where a mere carbon-dioxide reaction for the recognition of the hydrocarbon gas or vapor is to be attained (that is, when a quantitative combustion is not aimed at).

12. The proportion of finely divided metal used upon asbestos seems to be immaterial. Palladium asbestos containing 2 per cent. of palladium is nearly as efficient as that containing 30 per cent. As it is difficult to distribute the metal uniformly on the asbestos fiber, the higher percentage, by collecting irregularly, is more liable to cause glowing. Berliner[2] states (*a*) that the catalytic action of each metal, in the case of the reaction

$$H_2 + O = H_2O$$

begins at a fixed temperature and increases with rise of temperature; (*b*) that the oxidation-temperature for platinum foil is about 270°, for copper 280°, for zinc 350°, while aluminium has no action at 440°; and (*c*) that at constant temperatures the quantity of water formed is constant. My experiments do not confirm these statements.

[1] Wilm: Ber. d. chem. Ges. **25**, 220 (1892). [2] Ann. der Phys. Wied., n. F. **35**, 791 (1890).

Krause and Meyer[1] state that in the presence of mercury hydrogen begins to oxidize at 305°, while increasing temperature accelerates the oxidation. In contact with glass alone, hydrogen burns between the limits 650° and 730°.

Mixtures of Hydrogen with Air and Hydrocarbons.

A great number of experiments have been undertaken to ascertain the influence of hydrogen upon the oxidation of hydrocarbons in presence of metals. Of these the following is a summary: In a mixture of methane and air, a small proportion of hydrogen does not influence the oxidation of the methane provided the rate of flow of the gas-mixture over the palladium asbestos is very slow. Water will form readily, but no carbon dioxide, unless the temperature rises to about the melting-point of cadmium iodide (400°), that is to say, the temperature at which the methane would be oxidized if no hydrogen were present. If the gas-mixture flows rapidly, the burning hydrogen may so intensely heat the palladium as to cause it to glow. This involves an immediate production of carbon dioxide. With a slow movement of the gas, considerable volumes of hydrogen may be burned without formation of a trace of carbon dioxide. This is the conclusion reached by Hempel; but I have found the temperature at which the hydrocarbon is oxidized to be much higher than he supposes (about 200°). The same statement is true of hydrogen and ethane, and in general it may be said that the paraffins in presence of hydrogen and excess of air undergo oxidation by palladium asbestos only when the too rapid oxidation of the hydrogen causes glowing of the palladium.

The same general phenomena are observed in the case of mixtures of olefines and hydrogen with air. The temperatures of oxidation of the olefines are always lower than those of the corresponding paraffins. Below the temperature needed for oxidation a contraction in volume often occurs, due probably to occlusion by palladium. The addition of hydrogen to a mixture of air and carbon monoxide lowers the temperature of oxidation of the carbon monoxide by palladium asbestos. While the carbon monoxide alone was oxidized in air at temperatures above 300°, in presence of hydrogen it may yield carbon dioxide below 100°.

As has already been stated, the slow oxidation by palladium of a hydrocarbon in excess of air involves the conversion of carbon into carbon dioxide only, no carbon monoxide being produced.

[1] Ann. Chem. (Liebig) **264**, 85 (1891); Ber. d. chem. Ges. (Ref.) **24**, 698.

Experiments were made with a gaseous mixture having the following composition: Air, 94.9; propane, 3.1; hydrogen, 2. Oxidation of the paraffin occurred at temperatures varying from 270° to the melting-point of potassium nitrate (339°), but in no case was any carbon monoxide produced, nor could any olefines be detected in the gas after passing the palladium.

Action of Hydrocarbons upon Metallic Oxides.

As the temperature of oxidation by air in presence of finely divided metals seemed to vary within rather wide limits, it was possible that the differences might be due to a lack of absolutely uniform conditions in the various trials. So much care had been taken as regards the temperature and preparation of metal-coated asbestos that there was no positive ground for supposing that the apparatus and materials employed were in any way at fault.

Still further to study the matter, a series of trials was made of the temperature of reaction between reducing gases and the following compounds: oxide of copper, chromate of lead, oxide of silver, permanganate of silver, bichromate of silver. Only a few of the results need be cited here. Silver bichromate heated in ethylene yielded carbon dioxide at the following temperatures: (1), 320°; (2), 279°; (3), 300°; (4), 250°; (5), 265°; (7), 260°; (8), 280°. In each trial fresh silver bichromate was used. The results are, therefore, similar to those obtained with palladium asbestos. Barely visible traces of carbon dioxide were usually shown by the lime-water in advance of the strong reaction which occurred later. As in the case of oxidation by palladium in air, the hydrocarbon appears to undergo a kind of "smouldering" which changes rather suddenly as the temperature rises to a condition of much more intense oxidation.

Hempel has suggested that it might be possible, by a process of selective oxidation, to remove consecutively the various constituents of a mixture of combustible gases and in this way establish a method of analysis. The similarity in the properties of the various gases whose oxidation-temperatures I have studied, towards air and in presence of metals, as well as towards silver bichromate, seems to render doubtful the possibility of such a method. From this statement is to be excepted the determination of hydrogen, the methods for which have been so highly perfected by Hempel and Winkler.

[*To be continued.*]

Contributions from the Chemical Laboratory of Harvard College.

LXXXIII.—ON CERTAIN SUBSTITUTED CROTONOLACTONES AND MUCOBROMIC ACID.[1]

By Henry B. Hill and Robert W. Cornelison.

Several years ago a dichlorpyromucic acid was described by Hill and L. L. Jackson,[2] which differed from all the substituted pyromucic acids then known, in that it was readily decomposed by concentrated hydrochloric acid at 100° at ordinary pressures. Carbonic dioxide was evolved and a neutral body was formed which melted at 52°–53°, and contained a percentage of chlorine which corresponded to the formula $C_4H_4ClO_2$. A body of similar properties, melting at 77°, had previously been found in small quantity by Hill and Sanger[3] among the products formed from pyromucic tetrabromide by the action of an alcoholic solution of sodic hydrate. A complete analysis of this body had shown that its formula was $C_4H_5BrO_2$, but a lack of material rendered a detailed study of it impossible. While the chlorine derivative was more accessible, it was not more carefully studied by Hill and L. L. Jackson, since it was discovered only at the close of their investigation of the chlorpyromucic acids. They were also but partially successful in determining the constitution of the γ-dichlorpyromucic acid from which it was so easily formed. They showed that one chlorine atom of this acid was in the δ position, but could bring forward no definite facts to prove whether it was a $\beta\delta$-dichlorpyromucic acid stereometrically isomeric with the common form, or whether it was the third possible structural isomer, the $\gamma\delta$-dichlorpyromucic acid. In the former case its ready decomposition by aqueous hydrochloric acid might be due to its peculiar configuration; in the latter case this reaction might be conditioned by the simultaneous presence of halogens in the γ and δ positions. If the instability of the acid were due to the positions occupied by the halogen atoms, it seemed probable that the trisubstituted pyromucic acids which also contain halogen in the

[1] Presented to the American Academy. A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1893, by Robert W. Cornelison, then candidate for the degree of Doctor of Philosophy.

[2] Proc. Am. Acad. **24**. 348; This Journal **12**, 118.

[3] Proc. Am. Acad. **21**, 158.

γ and δ places would show the same behavior. Although Hill and Sanger had observed no such decomposition in studying tribrompyromucic acid, and Hill and L. L. Jackson noticed no such reaction with the trichlorpyromucic acid, in neither case had direct experiments in this direction been made, and it was quite possible that the decomposition in question had been overlooked. It was soon found, on trial, that tribrompyromucic acid was decomposed in analogous fashion, but that the reaction was effected with much more difficulty, so that a temperature materially above 100° was necessary in order to bring it about. When heated to boiling with concentrated hydrobromic acid, carbonic dioxide was evolved and a body melting at 90°–91° was formed, which showed a close resemblance to the monohalogenized bodies already known, and which had the similar formula $C_4H_2Br_2O_2$. From trichlorpyromucic acid the analogous body $C_4H_2Cl_2O_2$, melting at 50°–51°, could be made without difficulty. In studying the behavior of other substituted pyromucic acids under the same conditions, it was found that the $\beta\delta$-dibrompyromucic acid could also be made to undergo the same decomposition, although but a comparatively small yield of a body $C_4H_3BrO_2$, melting at 58°, could thus be obtained. This mode of decomposition was, therefore, not confined to those acids which contained halogen at the same time in the γ and δ positions. By following an entirely different method it was found that the $\beta\delta$-dibrompyromucic acid could be converted into an isomeric body, $C_4H_3BrO_2$, which melted at 77°, and was identical with that which had already been discovered by Hill and Sanger. The $\beta\delta$-dibrompyromucic acid was treated with bromine in aqueous solution, and the brommaleyl bromide, $C_4HBr_3O_2$, which, according to the observations of Hill and Sanger,[1] is thus formed, when carefully reduced by zinc-dust and glacial acetic acid, yielded the body melting at 77°. The mucobromyl bromide $C_4HBr_3O_2$ described by Hill and O. R. Jackson[2] was so simply related, as far as its empirical formula was concerned, to the body $C_4H_3Br_3O_2$ formed from tribrompyromucic acid, that it seemed possible to establish experimentally a direct connection between the two. It was found that mucobromyl bromide could readily be reduced by a variety of reducing agents, and that under certain conditions a nearly quantitative yield of the body $C_4H_3Br_3O_2$, melting at 90°–91°, could be obtained from it.

[1] Proc. Am. Acad. **12**, 166. [2] *Ibid.* **16**, 174.

Moreover, this reaction could be reversed and mucobromyl bromide obtained by the action of bromine upon this reduction-product. In the same way, by the reduction of mucochloryl bromide the body $C_4H_2Cl_2O_2$, melting at 50°–51°, which had been made from trichlorpyromucic acid, could readily be obtained in any desired quantity.

Since the several bodies already mentioned were evidently perfectly similar in their structure, we chose for more detailed study the body $C_4H_2Br_2O_2$, which was the most readily accessible. The melting-point of this substance, 90°–91°, was not far removed from that assigned (88°) by Toennies[1] to a body of like formula, which he obtained by the oxidation of $\beta\gamma$-dibrompyromucic acid with bromine-water, and it was not difficult to suppose the two bodies identical. Toennies published no analyses whatsoever of his product, and Hill and Sanger[2] were unable to obtain the substance in larger quantities; but according to their observations a preparation which gave the proper percentage of bromine melted at 89°–90°. A careful comparison of the substance prepared according to Toennies with that obtained by the decomposition of tribrompyromucic acid, or by the reduction of mucobromyl bromide, showed the two bodies to be identical in every respect. The formation of dibrommaleic acid by the prolonged action of nitric acid upon this body sufficiently established the relative position of the two bromine atoms and left for its constitution the choice between the following formulæ:

Toennies found that his product could be converted into mucobromic acid by oxidation with chromic acid, and therefore considered it to be the double aldehyde of dibromfumaric acid. We found, on the other hand, that the body showed none of the ordinary characters of an aldehyde. On warming with chromic acid it was slowly oxidized, but mucobromic acid was not formed in quantity sufficient to enable us to identify it with precision. On long boiling with bromine and water, mucobromic acid was formed. From concentrated nitric acid it could be recrystallized unchanged,

[1] Ber. d. chem. Ges. **12**, 1902.

[2] Proc. Am. Acad. **21**, 172.

and only after continued boiling was it oxidized to mucobromic and dibrommaleic acids. It did not combine with acid sodic sulphite, and did not react with hydroxylamine. Aniline in alcoholic solution removed one atom of bromine and gave a phenylamido derivative of the form $C_4H_2(C_6H_5NH)BrO_2$, and phenylhydrazine also removed bromine. Aqueous alkalies dissolved it with the formation of a deep yellow solution, but decomposition soon ensued with the elimination of hydrobromic acid. The whole behavior of the body was in direct opposition to the assumption that it was a double aldehyde, and the unsymmetrical structure was further established by the existence of two isomeric bodies of the same general constitution which contained a single bromine atom. The conclusion was inevitable that the body was a dibromcrotonolactone. The rigorous proof of its lactone-structure, through its conversion into a salt of the corresponding oxy-acid, was rendered difficult by the presence of the halogen, since the halogen itself was rapidly removed in alkaline solution. By adding a decinormal solution of potassic hydrate to a cold dilute solution of the substance, it is true that it was easy to prove that very nearly two molecules of potassic hydrate were neutralized in the reaction, while but one molecule of potassic bromide was formed, but it was impossible to isolate definite products of the decomposition. On reducing the body with zinc and dilute sulphuric acid the bromine was completely removed, and on distillation a feebly acid solution was obtained, which on titration with decinormal potassic hydrate proved to contain a lactone. By the usual methods an amorphous barium salt was obtained, which when thoroughly dried had the percentage composition required by a baric oxycrotonate. The isolation of the crotonolactone itself proved to be a matter of such difficulty that we attempted to find some derivative which would be more manageable. The bodies containing the aniline residue in place of one of the halogen atoms were found to be useless for our purpose, since they were decomposed by boiling in alkaline solution with the formation of phenyl isocyanide, and the phenylamidocrotonolactone formed from them by reduction was also decomposed with the formation of aniline under the same conditions. It seemed probable that the corresponding derivatives containing the phenoxy group would prove to be much more stable. While we have not yet succeeded in replacing the bromine of the body $C_4H_3Br_2O_2$ directly by the phenoxy group, we have had no diffi-

culty in preparing such a body by the reduction of the bromanhydride of the mucophenoxybromic acid which was described by Hill and Stevens.[1] The body thus formed was easily shown to be a phenoxybromcrotonolactone, since it dissolved in hot alkaline solutions with the formation of the salts of the corresponding oxyacid. On acidifying the well cooled alkaline solution the phenoxybromoxycrotonic acid was obtained, which was stable under ordinary conditions, but which was again converted into the lactone by heat. These results were fully confirmed by a study of the phenoxychlorcrotonolactone, which was prepared by the reduction of mucophenoxychloryl bromide. The position which the phenoxy group takes in entering mucobromic acid has already been shown with sufficient precision by Hill and Stevens, since a remarkably stable phenoxybromacrylic acid is readily formed from this product by the action of alkalies. The phenoxylactones containing halogen must therefore have the constitution

$$\begin{array}{l} BrC-CH_2 \\ \| \quad >O, \\ C_6H_5OC-CO \end{array} \qquad \begin{array}{l} ClC-CH_2 \\ \| \quad >O; \\ C_6H_5OC-CO \end{array}$$

and the analogous bodies containing halogen alone, the structure

$$\begin{array}{l} BrC-CH_2 \\ \| \quad >O, \\ BrC-CO \end{array} \qquad \begin{array}{l} ClC-CH_2 \\ \| \quad >O. \\ ClC-CO \end{array}$$

The formation of these bodies from tribrom- and trichlorpyromucic acids seems to us to be most readily explained by assuming that a trisubstituted furfuran is first formed with the loss of carbonic dioxide:

$$\begin{array}{l} XC=C-COOH \\ | \quad >O \\ XC=CX \end{array} = \begin{array}{l} XC=CH \\ | \quad >O + CO_2. \\ XC=CX \end{array}$$

This then adds a molecule of haloid acid with the shifting of the double bond in a manner identical with that observed by Von Baeyer and Rupe[2] in the reduction of dichlormuconic acid:

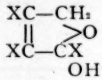
$$\begin{array}{l} XC=CH \\ | \quad >O \\ XC=CX \end{array} + \begin{array}{l} H \\ | \\ X \end{array} = \begin{array}{l} XC-CH_2 \\ \| \quad >O. \\ XC-CX_2 \end{array}$$

The addition-product is then decomposed by water, giving the

[1] Proc. Am. Acad. **19**, 262.

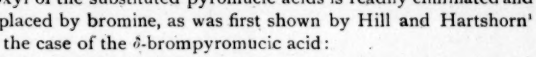
[2] Ann. Chem. (Liebig) **256**, 25.

lactone. Possibly a molecule of water is directly added to the trisubstituted furfuran, giving

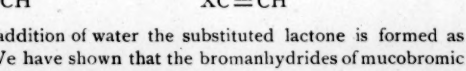


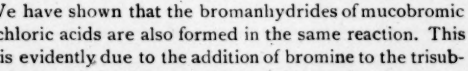
which would at once pass into the lactone by the loss of haloid acid.

The conversion of the $\beta\gamma$-dibrompyromucic acid into the dibrom-crotonolactone, and of the $\beta\gamma$-dichlorpyromucic acid into the corresponding dichlorcrotonolactone by the action of bromine in aqueous solution likewise finds its explanation in the formation of a trisubstituted furfuran. In aqueous acid or alkaline solution the carboxyl of the substituted pyromucic acids is readily eliminated and replaced by bromine, as was first shown by Hill and Hartshorn[1] in the case of the δ-brompyromucic acid:



By the addition of water the substituted lactone is formed as before. We have shown that the bromanhydrides of mucobromic and mucochloric acids are also formed in the same reaction. This formation is evidently due to the addition of bromine to the trisubstituted furfuran and the decomposition of this product by water:





It has already been said that two isomeric monosubstituted crotonolactones may be made by appropriate means from the disubstituted pyromucic acids containing the halogens in the β and δ positions. By heating these substituted pyromucic acids with mineral acids the brom- and chlorcrotonolactones melting at 58° and 26° respectively, may be made. The reaction is evidently perfectly analogous to the decomposition of the trisubstituted pyromucic acids under like conditions which has just been

[1] Ber. d. chem. Ges. **18**, 448.

discussed. The carboxyl group is replaced by hydrogen with the loss of carbonic dioxide, and the substituted furfuran thus formed then passes into the lactone as before:

$$\begin{array}{l} XC=C-COOH \\ \quad\vert\quad\ >O \\ HC=CX \end{array} = \begin{array}{l} XC=CH \\ \quad\vert\quad\ >O + CO_2 \\ HC=CX \end{array}$$

$$\begin{array}{l} XC=CH \\ \quad\vert\quad\ >O + H_2O \\ HC=CX \end{array} = \begin{array}{l} XC-CH_2 \\ \quad\Vert\quad\ >O + HBr. \\ HC-CO \end{array}$$

The β-substituted lactones which are thus formed may be made much more conveniently by the partial reduction of the disubstituted lactones. In order to prepare the monohalogenized crotonolactones with the halogen in the α-position from the $\beta\delta$-dichlor- and dibrompyromucic acids, derivatives of maleic acid must first be formed. The first step in the reaction is the formation of a trisubstituted furfuran through the replacement of the carboxyl by bromine:

$$\begin{array}{l} XC=C-COOH \\ \quad\vert\quad\ >O + Br_2 \\ HC=CX \end{array} = \begin{array}{l} XC=CBr \\ \quad\vert\quad\ >O + CO_2 + HBr. \\ HC=CX \end{array}$$

Through the addition of bromine with the shift of the double bond, as before,

$$\begin{array}{l} XC=CBr \\ \quad\vert\quad\ >O + Br_2 \\ HC=CX \end{array} = \begin{array}{l} XC-CBr_2 \\ \quad\Vert\quad\ >O; \\ HC-CXBr \end{array}$$

a body is formed which through the action of water yields the derivative of maleic acid:

$$\begin{array}{l} XC-CBr_2 \\ \quad\Vert\quad\ >O + H_2O \\ HC-CXBr \end{array} = \begin{array}{l} XC-CO \\ \quad\Vert\quad\ >O + 2HBr. \\ HC-CXBr \end{array}$$

This in its turn gives the lactone by reduction:

$$\begin{array}{l} XC-CO \\ \quad\Vert\quad\ >O. \\ HC-CH_2 \end{array}$$

In the case of the $\beta\delta$-dibrompyromucic acid, the tribromfurfuran, which should appear as the intermediate product in this reaction, has been isolated in a pure condition by Mr. W. M. Booth in this laboratory, and has been found to yield, when treated with bro-

mine in aqueous solution, the brommaleyl bromide described by Hill and Sanger.

The α-bromcrotonolactone may also be formed by the action of bromine in aqueous solution upon β-brompyromucic acid. The reaction is evidently identical with that through which the dibromcrotonolactone is formed from $\beta\gamma$-dibrompyromucic acid. A bibromfurfuran is first formed, which by the fixation of water and the elimination of hydrobromic acid passes into the lactone:

$$\begin{array}{l} BrC=C-COOH \\ \quad\quad | \quad\quad >O + Br_2 \\ HC=CH \end{array} = \begin{array}{l} BrC=CBr \\ \quad\quad | \quad\quad >O + CO_2 + HBr; \\ HC=CH \end{array}$$

$$\begin{array}{l} BrC=CBr \\ \quad\quad | \quad\quad >O + H_2O = \\ HC=CH \end{array} \begin{array}{l} BrC-CO \\ \quad\quad || \quad\quad >O + HBr. \\ HC-CH_2 \end{array}$$

The isomerism observed in the monohalogenized crotonolactones must be due to the position of the halogen atoms, since, according to the views at present held concerning geometric isomerism, lactones can be formed from the maleïnoid forms only. A definite proof that the halogen atoms in the α- and β-bromcrotonolactones are attached to different carbon atoms is easily given. The $\alpha\beta$-dibromcrotonolactone yields with hydriodic acid an iodine derivative which can be reduced to β-bromcrotonolactone. This same iodine compound gives with aniline a phenylamidobromcrotonolactone which on reduction is converted into the same phenylamidocrotonolactone that may be made by the action of aniline upon the α-bromcrotonolactone:

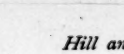
$$\begin{array}{l} BrC-CH_2 \\ \quad\quad || \quad\quad >O \\ IC-CO \end{array} \rightarrow \begin{array}{l} BrC-CH_2 \\ \quad\quad || \quad\quad >O \\ HC-CO \end{array}$$

$$\begin{array}{l} BrC-CH_2 \\ \quad\quad || \quad\quad >O \\ C_6H_5.NH.C-CO \end{array} \rightarrow \begin{array}{l} HC-CH_2 \\ \quad\quad || \quad\quad >O \\ C_6H_5.NH.C-CO \end{array}$$

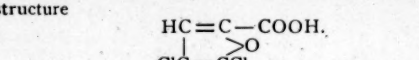
$$\begin{array}{l} HC-CH_2 \\ \quad\quad || \quad\quad >O \\ BrC-CO \end{array}$$

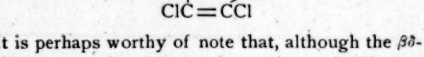
It is evident that the acid described by Hill and L. L. Jackson under the provisional name of the χ-dichlorpyromucic acid, since it readily gives the α-chlorcrotonolactone on decomposition with

mineral acids, must in fact be the $\gamma\delta$-dichlorpyromucic acid, and its structure

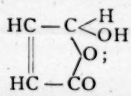


It is perhaps worthy of note that, although the $\beta\delta$- and the $\gamma\delta$-dichlorpyromucic acids give the two isomeric chlorcrotonolactones when heated with acids, they give the same α-chlorcrotonolactone when they are treated with bromine in aqueous solution, and the resulting product it reduced. Evidently two isomeric dichlorbromfurfurans are first formed, which yield the corresponding addition-products with bromine, but these addition-products are attacked by water in such a way that in each case the chlorine is left in the α-position with regard to the oxidized carbon:

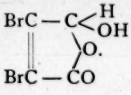




The close relationship between mucobromic acid and the bodies which have thus been shown to be derivatives of crotonolactone, naturally recalled the suggestions which had already been made as to the constitution of mucobromic acid itself. As early as 1882 Roser[1] pointed out that the so-called fumaric aldehyde-acid of Limpricht might in reality be an oxylactone,



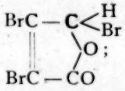
and afterward, in 1887, Anschütz,[2] in his interesting and suggestive discussion of the constitution of maleic and fumaric acids, was led to the conclusion that mucobromic acid was an oxydibromcrotonolactone:



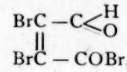
[1] Ber. d. chem. Ges. **15**, 1593.

[2] Ann. Chem. (Liebig) **239**, 161.

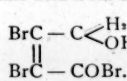
It was evident that the almost quantitative reduction of mucobromyl bromide by such a reducing-agent as stannous chloride in the cold, was perfectly intelligible if the formula of this bromide were



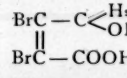
while the formation of a lactone under these conditions from the bromanhydride derived from the aldehyde-acid,



could hardly be explained except by assuming that the aldehyde group was itself first attacked, and the lactone then formed by the elimination of hydrobromic acid from the body



This explanation seemed to us exceedingly improbable, and we furthermore showed by direct experiment that no perceptible amount of the dibromcrotonolactone could be formed by the action of stannous chloride and hydrochloric acid upon mucobromic acid itself, or by its reduction with zinc and acetic acid, while the alcohol-acid,

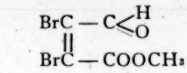


which would be formed if the aldehyde group were readily reduced, would certainly yield the lactone with facility. The ready formation of mucobromyl bromide by the action of bromine at 100° upon the dibromcrotonolactone, seemed equally conclusive, and the lactone formula for mucobromyl bromide established. Since phosphorous tribromide converts mucobromic acid almost quantitatively into its bromanhydride, the lactone structure of mucobromic acid itself seemed to be proved. It can hardly be supposed that a bromide of the lactone formula could be formed from the aldehyde-acid, for this would imply the replacement of

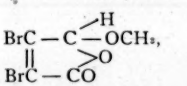
the aldehyde oxygen through the phosphorous tribromide, leaving the hydroxyl of the carboxyl group to form the lactone by the elimination of hydrobromic acid. Although Hill and O. R. Jackson[1] showed many years ago that mucobromic acid could readily be converted into dibrommaleic acid by means of argentic oxide, it was evident that even this mode of oxidation no longer warranted a definite conclusion as to its aldehyde character. We therefore thought it necessary to take up the study of the behavior of mucobromic and mucochloric acids, as well as the related acids containing the phenoxy group, toward hydroxylamine. We found that these four acids gave oximes with ease, and in studying more in detail the compounds formed from mucobromic acid we found that they were perfectly analogous to the bodies formed by the action of hydroxylamine upon opianic, phthalaldehydic, and pseudopianic acids, as described by Lieberman,[2] Allendorf,[3] Racine,[4] and Perkin.[5] Mucobromoxime is so unstable that it passes spontaneously into its anhydride, and can be formed only by the action of free hydroxylamine in aqueous solution. The anhydride is formed through the hydrochlorate in alcoholic solution, and by boiling this alcoholic solution or by heat alone is converted into dibrommaleïnimide. The oxime or its anhydride is further converted into the acid ammonium salt of dibrommaleic acid by boiling it with water. The ready formation of oximes of perfectly normal character from mucobromic acid would in itself naturally be considered as establishing the aldehyde character of this acid. Still the difficulty in explaining the conversion of the bromanhydride of an aldehyde-acid into a lactone by reduction with stannous chloride in the cold, is so great that it seems to us more rational to suppose either that hydroxylamine acts directly upon an oxylactone of this type and that the ordinary oxime is then formed by molecular rearrangement, or that under the conditions of the reaction the hydroxylamine acts only through the fixation of a molecule of water, and the breaking of the lactone ring with formation of the aldehyde-acid.

In this connection we were interested to know whether the esters of mucobromic acid would enter into reaction as readily as the free acid. While it seemed probable that the ester of the aldehyde-acid of the form

[1] Proc. Am. Acad. **16**, 186. [2] Ber. d. chem. Ges. **19**, 2278, 2923. [3] *Ibid.* **24**, 3264.
[4] Ann. Chem. (Liebig) **239**, 81. [5] J. Chem. Soc. **57**, 1069.



would be attacked by hydroxylamine quite as readily as the free acid; the ester formed from the oxylactone,



might well prove more refractory. Several years ago Lieberman[1] tried the behavior of the ethyl ester of opianic acid with hydroxylamine, and obtained only the opianic oxime anhydride. We have been able to find described no other experiments with the esters of the acids in question. Our own experiments with mucobromic acid, and its methyl ester, showed that the ester was attacked with much more difficulty. While mucobromic acid is rapidly converted into its oxime and oxime anhydride, we failed to discover any appreciable action when hydroxylamine is added to a solution of methyl mucobromate in methyl alcohol at ordinary temperatures, even after the lapse of several days. On boiling, the methyl ester of mucobromoxime was formed, identical with the body formed by heating mucobromoxime with methyl alcohol. Further experiments in this direction can alone show whether the difference in behavior between the acids of this series and their esters is sufficiently general to warrant definite conclusions as to their structure. The action of phenylhydrazine upon mucobromic and mucochloric acids and their esters, which we hoped to study in detail, proved to yield bodies which were not suitable for investigation.

Many years ago Mr. C. W. Andrews, who was at that time an assistant in this laboratory, made some experiments as to the action of aniline upon mucobromic acid and its ethyl ester, which he was unable to complete at the time, and which have never been published. He found that the reaction with mucobromic acid was complex, in that bromine was partially replaced by the aniline residue, and also that oxygen was eliminated by condensation. In marked contrast with this reaction was the behavior of ethyl mucobromate with aniline. One atom of bromine was

[1] Ber. d. chem. Ges. **19**, 2936.

here replaced, but the rest of the molecule remained unaltered, so that the body $C_4H_3Br(NHC_6H_5)O_3C_2H_5$ was formed in nearly theoretical quantity. It therefore seemed to us of interest to determine whether ethyl mucobromate would behave in an analogous way with ammonia. We found, however, in this case, that the reaction took a different course, and that the ethoxy group was first attacked. The body which is thus formed has the formula of the amide of mucobromic acid, but its behavior is in some respects anomalous. It dissolves readily in caustic alkalies, and may be reprecipitated unchanged by immediate acidification. It is but slowly converted into mucobromic acid by boiling with mineral acids, and with oxidizing agents it yields dibrommaleïnimide. From mucochloric acid a body of similar properties was obtained.

$\alpha\beta$-Dibromcrotonolactone.

Although tribrompyromucic acid is little affected by boiling hydrochloric acid, it is quite readily decomposed, with the escape of carbonic dioxide, when heated to 130° with diluted sulphuric acid (sp. gr. 1.43), or when boiled with concentrated hydrobromic acid. The reaction seemed to be more neatly effected with the latter reagent, and we therefore heated tribrompyromucic acid with from four to five times its weight of concentrated hydrobromic acid with a return-condenser. When no further escape of carbonic dioxide could be detected, the somewhat dark-colored clear solution was cooled, and diluted with water. A heavy crystalline precipitate was thus thrown down, which could easily be purified by recrystallization from alcohol or ligroïn. The crude product obtained in this way amounted to about half the weight of the tribrompyromucic acid taken. Analyses of the body after several recrystallizations from alcohol showed that it had the formula $C_4H_3Br_3O_2$. For the analyses of this dibromcrotonolactone, and of several of its derivatives, which we publish, we are indebted to Mr. H. N. Herman, who made a preliminary study of this body some two years ago, but was unable to continue the investigation.

I. 0.2472 gram substance gave 0.1788 gram CO_2 and 0.0209 gram H_2O.

II. 0.2394 gram substance gave 0.3711 gram AgBr.

	Calculated for $C_4H_2Br_2O_2$.	Found. I.	II.
C	19.83	19.73	...
H	0.83	0.94	...
Br	66.12	...	65.96

This same body may also be made directly from mucobromic acid by the action of phosphorous iodide. Phosphorus is dissolved in five times its weight of carbonic disulphide, equivalent weights of iodine and mucobromic acid well ground together, are then added, and the nearly solid mass heated on the water-bath with reverse-cooler. The reaction sets in slowly and, frequently, only after a part of the carbonic disulphide has been allowed to escape through the cooler. With no solvent present the reaction is violent and yields little or no product. When the mass is completely liquefied, the rest of the carbonic disulphide is distilled off, the flasked well cooled, and cold water added in not too small quantity. On shaking, the crude lactone separates in a granular condition. In this way it is easy to obtain a product which amounts to two-thirds of the weight of the mucobromic acid taken, but it contains a decided percentage of iodine, and the preparation of pure dibromcrotonolactone from it is a matter of great difficulty. By fractional crystallization from various solvents we found it impossible to eliminate the iodine, but on distillation with steam the substance first carried over contained but little, and the percentage of iodine did not become large until about one-half of the material taken had passed over. The material which had thus been partially purified by fractional distillation with steam, could not be further purified by recrystallization, but after boiling for some time with bromine-water the iodine compound was oxidized, and a substance was then obtained which after several recrystallizations from alcohol possessed the properties and the composition of pure dibromcrotonolactone.

0.2439 gram substance gave 0.3779 gram AgBr.

	Calculated for $C_4H_2Br_2O_2$.	Found.
Br	66.12	65.93

The dibromcrotonolactone can much more readily be made from mucobromic acid by the reduction of its bromanhydride. Mucobromyl bromide was described many years ago by Hill and O. R. Jackson,[1] who made it by the action of phosphoric penta-

[1] Proc. Am. Acad. 16, 174.

bromide upon mucobromic acid. We have found that phosphorous tribromide is in many respects more advantageous for its preparation. The reaction runs somewhat slowly at 100°, but so smoothly that one molecule of the tribromide is sufficient for three molecules of mucobromic acid, and the yield is about 90 per cent. of the theoretical amount. After the reaction is over the flask is well cooled, cold water is added, and the whole vigorously shaken until the oil which first separates solidifies in a granular form. The crude product melts at 54°–55°, and by repeated recrystallization from small quantities of hot alcohol this melting-point may be raised to 56°–57°, one degree higher than the point given by Hill and O. R. Jackson. We attempted to purify the crude product by distillation *in vacuo*, but we found that the melting-point was depressed rather than raised by this treatment. We have not further studied the change which is thus apparently brought about by distillation, for we soon found that a perfectly pure dibromcrotonolactone could be made directly from the mucobromyl bromide, as it was precipitated by water, while it was difficult, if not impossible, to do this with the distilled substance of low melting-point. Hydriodic acid, or zinc-dust with glacial acetic acid, reduces the mucobromyl bromide to the lactone, although the former reagent yields a product which contains iodine. A far more efficient and convenient reducing-agent we found to be stannous chloride with hydrochloric acid, since this gives at once an essentially pure product in satisfactory quantity. Mucobromyl bromide is added to an equal weight of stannous chloride dissolved in the same amount of concentrated hydrochloric acid. The reduction proceeds rapidly with the evolution of heat, although in working with small quantities the reaction is greatly facilitated by warming gently at first. When the melting-point of the mucobromyl bromide is reached, the flask must be well shaken until the oil has completely disappeared. As the solution cools the dibromcrotonolactone crystallizes out, and still more separates on dilution. The yield which may be obtained in this way amounts to from 75 to 80 per cent. of the weight calculated from the mucobromyl bromide taken, or about 70 per cent. of that theoretically required by the mucobromic acid employed. A single recrystallization from alcohol is sufficient for its complete purification.

Dibromcrotonolactone is very sparingly soluble in cold water,

and dissolves in from 30 to 40 times its weight of boiling water. As the hot aqueous solution cools, the lactone crystallizes in small six-sided plates, or in pointed prisms crossing at an angle of 60°. From alcohol, in which it is somewhat sparingly soluble at ordinary temperatures, although very readily soluble on heating, it crystallizes in bundles of long friable prisms. From concentrated nitric acid it crystallizes in large, clear, brilliant oblique prisms. In boiling ligroïn it dissolves somewhat sparingly on boiling, and as the solution cools the greater part of it separates in finely felted needles. It is readily soluble in chloroform or benzol, more sparingly soluble in ether or carbonic bisulphide. It melts at 90°–91°, and boils, under a pressure of 18 mm., at 145°. With steam it volatilizes rapidly. Although it is remarkably stable in acid solutions, it is easily attacked by alkalies. The alkaline hydrates dissolve it, forming deep yellow solutions, and at the same time alkaline bromides are formed. In studying the action of decinormal potassic hydrate in the cold, we have found that approximately two molecules of potassic hydrate are neutralized by each molecule of the lactone taken, while but one molecule of potassic bromide is formed; but have been able to isolate no definite products of the reaction. The lactone was not attacked by hydroxylamine; with aniline it yielded, with the elimination of bromine, the well crystallized aniline derivative which will be described later. Phenylhydrazine also removed bromine, but gave no well characterized product.

Dibromfumaric Aldehyde of Toennies.

The melting-point and other properties of the dibromcrotonolactone recalled a body of like composition which was obtained in 1879 by Toennies,[1] through the action of bromine-water upon $\beta\gamma$-dibrompyromucic acid. He gives no analytical data to support his formula, and apparently had but small quantities of material at his disposal. From its behavior he considered the body to be the aldehyde of mucobromic acid, or the double aldehyde of dibromfumaric acid. In 1886 Hill and Sanger[2] again prepared this body from $\beta\gamma$-dibrompyromucic acid, but were unable to obtain it in satisfactory quantities, and hoped to return to it at some future time. A further study of the reaction has shown us that it is by no means simple in its nature. While we have been

[1] Ber. d. chem. Ges. **12**, 1902. [2] Proc. Am. Acad. **21**, 172.

unable to obtain a satisfactory yield of the desired product, we have succeeded in preparing an amount amply sufficient for its identification, and at the same time we have isolated a second product of the reaction.

Preliminary experiments showed us that it was most advantageous to add about 20 per cent. more than one molecule of bromine to the finely divided dibrompyromucic acid suspended in 20 times its weight of cold water. We therefore boiled 5 grams of pure $\beta\gamma$-dibrompyromucic acid with 100 cc. of water, and quickly cooled the solution in order to obtain the acid in a finely divided condition. When the temperature reached 16°, 1.2 cc. of bromine were added, and the whole well shaken. The color of the bromine gradually faded, but when it had completely disappeared a considerable amount of a well crystallized body remained undissolved. Instead of allowing the solution to stand over night, as Hill and Sanger had done, we filtered out the insoluble substance at the end of three hours, and extracted the colorless aqueous solution thoroughly with ether. The ethereal extract left on distillation a syrupy residue, which partially solidified on standing over night *in vacuo* over sulphuric acid. The crystals when thoroughly drained upon the pump and pressed weighed 0.85 gram. Two crystallizations from small quantities of hot alcohol yielded 0.65 gram of substance, which melted at 90°–91°, and showed the characteristic behavior of the dibromcrotonolactone. In order to identify it with precision, we converted it into the α-iodo-β-bromcrotonolactone, which is fully described later, by heating it with hydriodic acid, and found the product to melt at the proper point, 118°–119°. On reduction with zinc and acetic acid it yielded the β-bromcrotonolactone melting at 57°–58°, and with aniline the α-phenylamido-β-bromcrotonolactone with its characteristic properties, both of which bodies, as we shall afterwards show, may be made in the same way from the dibromcrotonolactone. As we shall show more fully later, we were unable to confirm the statement of Toennies that the dibromcrotonolactone could easily be converted into mucobromic acid by oxidation with chromic acid. By the action of bromine in aqueous solution a part of the $\beta\gamma$-dibrompyromucic acid had been converted into dibromcrotonolactone, according to the equation given by Toennies,

$$C_5H_4Br_2O_3 + Br_2 + H_2O = C_4H_2Br_2O_2 + CO_2 + 2HBr.$$

The viscous oil which had been drained from the crystalline product deposited a few more crystals of the lactone on long standing, but we have not yet examined it further. The insoluble matter, which had been removed by filtration before the extraction with ether, was washed with a dilute solution of sodic carbonate. But a small amount dissolved, and upon acidification 0.2 gram of a sparingly soluble acid was precipitated, which melted at 189°–190°, and was evidently unaltered dibrompyromucic acid. The residue, insoluble in the alkaline solution, weighed 1 gram, and consisted chiefly of mucobromyl bromide. It gave in alcoholic solution a deep blue evanescent color on the addition of sodic carbonate, and one crystallization from alcohol was sufficient to raise the melting-point to 56°–57°. A part of the dibrompyromucic acid had therefore been decomposed according to the equation

$$C_5H_4Br_2O_4 + 2Br_2 + H_2O = C_4HBr_3O_2 + CO_2 + 3HBr.$$

Mucobromyl bromide is so slowly attacked by water that little mucobromic acid could have been formed under the conditions chosen; but it is found in abundance when the product of the reaction stands for a long time in dilute solution. The alcoholic mother-liquors obtained from the recrystallization of the muçobromyl bromide were evaporated, and the residue boiled with water under a reverse-cooler until the bromanhydride had been converted into mucobromic acid. A small amount of insoluble material was then left, which had the odor of tetrabromfurfuran, but we were unable to identify it with precision. A preliminary experiment under essentially the same conditions had already yielded us a crystalline body, which was proved by its melting-point (64°), and other characters, to be tetrabromfurfuran. Hill and Sanger[1] had previously found that this substance was formed in considerable quantities when bromine was gradually added to the dibrompyromucic acid suspended in water.

Action of Oxidizing Agents.

As we already have said, dibromcrotonolactone may be crystallized without alteration from concentrated nitric acid, but on long boiling it is slowly oxidized, and mucobromic acid or dibrom-

[1] Proc. Am. Acad. 31, 172.

maleic acid formed. Even fuming nitric acid attacks it with difficulty, and after boiling for half an hour the greater part of the lactone taken may be recovered unchanged. We dissolved the lactone in 8 times its weight of concentrated nitric acid (sp. gr. 1.42), and boiled the solution for three hours under a reverse-condenser. The unaltered lactone was then driven off with steam, and the acid solution evaporated to small volume. On cooling, mucobromic acid separated in abundance, which melted at 119°–120°, after recrystallization from hot water. Even after boiling for six hours with concentrated nitric acid the oxidation was far from complete, but it was then easy to establish the formation of dibrommaleic acid through the melting-point (114°–115°) of its anhydride. On boiling the lactone with bromine-water, it is slowly converted into mucobromic acid. The reaction may be hastened greatly by using concentrated hydrobromic acid as a solvent, and the oxidation is then completed in a comparatively short time. The mucobromic acid which we obtained, when recrystallized from water, melted at 120°–121°. With chromic acid the action is also very slow, and we have been unable to identify any products of the oxidation except carbonic dioxide. If an amount of chromic acid was used which corresponded to one atom of oxygen for each molecule of the lactone, several hours at 100° were needed for the complete reduction of the chromic acid. On distillation large quantities of the unaltered lactone were obtained (melting-point 90°–91°), and the retort-residue, when evaporated to small volume, deposited nothing on cooling. This residue was therefore extracted with ether, the ethereal extract shaken with a dilute solution of sodic carbonate, and this alkaline solution immediately acidified with hydrochloric acid, and again extracted with ether. The ether then left upon evaporation a small syrupy residue, which was strongly acid to test-paper. After standing for several days, several minute clusters of rhombic plates could be seen under the microscope. In appearance they closely resembled mucobromic acid, but they were insufficient in quantity even for a melting-point determination. Since the dibromcrotonolactone reduced an ammoniacal solution of argentic nitrate on heating, we made one attempt to effect its oxidation with argentic oxide. On boiling an aqueous solution of the lactone with a large excess of well washed argentic oxide, metallic silver was formed, but at the same time argentic bromide in large quantity. An approximate quantitative deter-

mination showed that 87.5 per cent. of the total bromine contained in the lactone had been converted into argentic bromide. After a careful search we failed to find any products of the oxidation except an amount of dibrommaleic acid which was just sufficient for its complete identification through the microscopic appearance of its barium salt and the melting-point of its anhydride, 114°–115°.

Action of Bromine.

Dibromcrotonolactone is not attacked by bromine at ordinary temperatures, but at 100° substitution is quite rapidly effected. If equal molecules of bromine and the lactone are taken, a colorless oil is obtained after several hours' heating, which on standing gradually solidifies, and the crystalline solid may be purified by recrystallization from small quantities of alcohol. The substance which was thus obtained melted at 56°–57°, and gave with alkalies in alcoholic solution the characteristic blue color described by Hill and O. R. Jackson.[1] Mucobromyl bromide had therefore been formed from the dibromcrotonolactone according to the equation

$$C_4H_2Br_2O_2 + Br_2 = C_4HBr_3O_2 + HBr.$$

When heated with an excess of bromine further substitution is effected and a product is obtained in which both the hydrogen atoms of the dibromcrotonolactone are replaced. For the preparation of this body we heated equal molecules of mucobromyl bromide and bromine in a sealed tube at 125°–130°. At this temperature the reaction proceeds rapidly, but it is also completed at 100° on longer heating. The colorless oil which we obtained gave no blue color in alcoholic solution with sodic carbonate, and on standing gradually solidified. The carefully pressed solid proved to be extremely soluble in alcohol, ether, chloroform, benzol, or carbonic disulphide, but it was somewhat more sparingly soluble in ligroïn and could be purified by recrystallization from this solvent. The percentage of bromine which the substance contained corresponded to the formula $C_4Br_4O_2$.

I. 0.1685 gram substance gave 0.3177 gram AgBr.

II. 0.1884 gram substance gave 0.3552 gram AgBr.

	Calculated for $C_4Br_4O_2$.	Found. I.	II.
Br	80.00	80.23	80.20

[1] Proc. Am. Acad. **16**, 175.

This substance crystallizes from ligroïn in clustered leaflets which melt at 58°–59°. It has a strong suffocating odor like that of the acid bromanhydrides. When heated with water it is slowly dissolved and the solution then contains dibrommaleic acid. The acid was as usual identified by the crystalline form of the barium salt, and by the melting-point (114°–115°) of its anhydride. On treating the body with stannous chloride and hydrochloric acid the dibromcrotonolactone is again formed by reduction. The mode of formation, the composition, and the behavior of this body justify the conclusion that it is the unsymmetrical form of dibrommaleyl bromide. Its behavior will be further studied in this laboratory. We have made many unsuccessful attempts to prepare an identical or an isomeric body directly from dibrommaleic acid. We have tried the action of phosphoric pentabromide upon dibrommaleic anhydride at temperatures which varied from 100° to 225°, and either obtained the unaltered anhydride, or else carbonization ensued. We were equally unsuccessful in our attempts to prepare such a product through the salts of the acid.

Action of Aniline.

Aniline reacts upon the $\alpha\beta$-dibromcrotonolactone at ordinary temperatures and forms α-phenylamido-β-bromcrotonolactone. This substance is most readily prepared by dissolving the lactone in twenty parts of alcohol, diluting this solution with an equal weight of water, and then adding somewhat more than two molecules of aniline. On standing, long needles of the aniline derivative separate in abundance, which may be purified by recrystallization from 60-per cent. acetic acid, and afterward from alcohol.

I. 0.2570 gram substance gave 0.4426 gram CO_2 and 0.0763 gram H_2O.

II. 0.2393 gram substance gave 0.1775 gram AgBr.

III. 0.2727 gram substance gave 13.4 cc. moist nitrogen at 21° and 763 mm.

	Calculated for $C_{10}H_8BrNO_2$.	Found. I.	II.	III.
C	47.24	46.97	...	...
H	3.15	3.30	...	...
Br	31.50	...	31.56	...
N	5.51	...	...	5.63

α-Phenylamido-β-bromcrotonolactone is almost insoluble in ether, carbonic disulphide, or ligroïn, but dissolves somewhat

more readily in boiling benzol or chloroform. It is somewhat sparingly soluble even in boiling alcohol, still less freely in boiling water, and as the solutions cool is deposited in each case in long brilliant needles. In hot glacial acetic acid the substance dissolves readily; from chloroform it crystallizes in thin transparent plates. When slowly heated it melts with decomposition at about 165°, but if the capillary tube containing the substance is plunged into the heated bath it melts promptly at 186°–187° and immediately decomposes. In alkaline solutions it dissolves readily on warming, and if the solution be quickly cooled it crystallizes out apparently unchanged, but on heating for a longer time decomposition ensues, as the strong odor of phenyl isocyanide shows. By the action of sodium amalgam bromine is removed and α-phenylamidocrotonolactone, which we shall describe later, is formed. We have been unable to replace the second atom of bromine by heating with an excess of aniline.

Action of Hydriodic Acid.

When αβ-dibromcrotonolactone is dissolved in ordinary distillable hydriodic acid and the solution is boiled for a short time, or heated for a longer time at 100°, one atom of bromine is replaced by iodine, and as the solution cools the α-iodo-β-bromcrotonolactone separates in long prisms. This same body is also formed by the action of phosphorous iodide upon mucobromic acid or when hydriodic acid acts upon mucobromyl bromide, and it may easily be made the chief product of the latter reaction. For analysis it was recrystallized from alcohol.

I. 0.2393 gram substance gave 0.1453 gram CO_2 and 0.0229 gram H_2O.

II. 0.1874 gram substance gave 0.2747 gram AgBr + AgI.

III. 0.2031 gram substance gave 0.2978 gram AgBr + AgI.

	Calculated for $C_4H_2BrIO_2$.	Found. I.	II.	III.
C	16.61	16.56	...	...
H	0.69	1.05	...	...
Br + I	71.63	...	71.76	71.78

The α-iodo-β-bromcrotonolactone is quite readily soluble in benzol or chloroform, more sparingly soluble in ether, carbonic disulphide, or ligroïn. It dissolves freely in boiling alcohol, and

as the solution cools is deposited in quite large, oblique, colorless prisms, which gradually change color on exposure. With steam it distils with difficulty. The melting-point of most preparations of this substance we have found to be constant at 118°–119°. Still we were frequently unable to raise by recrystallization alone the melting-point of material which melted at too low a temperature, and on one occasion a preparation made in the usual way melted one degree higher, at 119°–120°. Toward aqueous alkalies this substance behaves like the corresponding bromine derivative, an alkaline iodide being formed in the decomposition. Concentrated nitric acid or bromine-water on boiling liberates iodine. When heated with one molecule of dry bromine in a sealed tube at 100°, iodine is also liberated, and but a small quantity of hydrobromic acid is formed. With aniline in dilute alcoholic solution it yields the α-phenylamido-β-bromcrotonolactone which has already been described, although not quite as smoothly as the dibromlactone, since dark-colored viscous products, which we have not further examined, are formed at the same time. On reduction with zinc-dust and glacial acetic acid, the β-bromcrotonolactone melting at 58°, which we shall presently describe, was formed. After dilution with water the acid solution was extracted with ether, the ethereal extract washed with a dilute solution of sodic carbonate, and the crystalline residue obtained by the evaporation of the ether recrystallized several times from small quantities of alcohol. The body thus obtained had the properties of the β-bromcrotonolactone, melted at 57°–58°, contained but an unweighable trace of iodine, and gave on analysis the required percentage of bromine:

0.2078 gram substance gave 0.2407 gram AgBr.

	Calculated for $C_4H_3BrO_2$.	Found.
Br	49.08	49.27

When the iodobromcrotonolactone was boiled with hydriodic acid the separation of iodine soon ensued. After long boiling with the addition of red phosphorus, although traces of volatile products which had the odor of fat acids had been formed, the main product of the reduction was a viscous oily body, which could be extracted by ether from the diluted solution, but from which we were unable to prepare any material suitable for analysis. With distillable hydriodic acid and red phosphorus

in sealed tubes at temperatures below 180° we obtained substantially the same result, while prolonged heating at 200° brought about decomposition. We had no better success when we employed hydriodic acid saturated at 0°, although in this case decomposition set in at a lower temperature.

β-Bromcrotonolactone.

When βδ-dibrompyromucic acid is boiled with concentrated hydrobromic acid, it is slowly decomposed, carbonic dioxide is evolved, and β-bromcrotonolactone is formed. The reaction does not run as smoothly as it does with tribrompyromucic acid, and more or less carbonization ensues. When the reaction appears to be completed, the dilution of the dark brown solution usually precipitates a small amount of dark-colored unaltered acid, but no lactone is thus thrown down. The filtered solution is then extracted with ether, the ethereal extract washed with a dilute solution of sodic carbonate, and dried with calcic chloride. The residue left after distilling off the ether gradually solidifies on standing, and the crude product, which amounts to about one quarter of the dibrompyromucic acid taken, may be recrystallized from small quantities of alcohol or from ether. The same body may be prepared much more conveniently by the reduction of the αβ-dibromcrotonolactone with zinc-dust and acetic acid. The dibromcrotonolactone is suspended in its own weight of 80-per cent. acetic acid, and somewhat more than the calculated weight of zinc-dust is then added with careful cooling. At first the reduction proceeds rapidly with the evolution of heat, but several hours at ordinary temperatures are necessary for its completion. When the zinc has nearly disappeared the viscous solution is warmed, filtered, and the clear filtrate cautiously diluted with water. The bromlactone is thus precipitated as an oil, which after cooling and shaking soon solidifies in the form of colorless feathery crystals. The precipitated lactone amounts to 45 per cent. of the weight of the dibromcrotonolactone taken, and somewhat more may be obtained by extracting the mother-liquor with ether.

I. 0.2417 gram substance gave 0.2609 gram CO_2 and 0.0440 gram H_2O.

II. 0.1913 gram substance gave 0.2214 gram AgBr.

	Calculated for $C_4H_3BrO_2$.	Found. I.	II.
C	29.45	29.44	...
H	1.86	2.02	...
Br	49.08	...	49.24

The β-bromcrotonolactone is readily soluble in alcohol, chloroform, benzol or carbonic disulphide. It is decidedly less soluble in ether, and very sparingly soluble in ligroïn. From small quantities of alcohol it crystallizes in colorless clustered prisms, from ether by slow evaporation in large transparent six-sided plates. It is quite readily soluble in hot water, and as the hot aqueous solution cools it separates in clear obliquely truncated prisms. It melts at 58°, and boils, under a pressure of 18 mm., at 140°. It distils with steam, although with some difficulty. Aqueous alkalies dissolve it with the formation of a deep yellow color, and the solution then contains an alkaline bromide. In dilute alcoholic solution aniline also removes bromine, but forms at the same time a dark-colored viscous oil, from which we have been able to isolate no crystalline product.

Action of Bromine.

β-Bromcrotonolactone is but slowly attacked by bromine in the cold. If one molecule of bromine is added to the powdered lactone, a clear deep red solution is soon obtained, but the color fades so slowly that several days are required to complete the reaction at ordinary temperatures. On opening the tube a small quantity of hydrobromic acid escaped, but the weight of the crystalline product was substantially the same as that of the materials employed. After several recrystallizations from alcohol an analysis also showed that the substance had been formed by the addition of bromine:

0.2965 gram substance gave 0.5175 gram AgBr.

	Calculated for $C_4H_3Br_3O_2$.	Found.
Br	74.30	74.27

This body, which from the mode of its formation must be the $\alpha\beta_2$-tribrombutyrolactone, is readily soluble in alcohol, ether, benzol, carbonic disulphide, or chloroform, but is more sparingly soluble in ligroïn. From alcohol it is deposited in large, well-formed, brilliant prisms, which melt at 63°–64°. On boiling with water a

part distils unchanged, but decomposition soon sets in, carbonic dioxide is evolved, and hydrobromic acid is formed. If the β-bromcrotonolactone is heated to 100° with one molecule of bromine, the color of the bromine soon disappears, but at the same time hydrobromic acid is formed in considerable quantities. With an excess of bromine at 100° mucobromyl bromide is formed in abundance. The product which we obtained melted at 56°–57°, gave in alcoholic solution a deep blue color with sodic carbonate, and when heated with water yielded mucobromic acid.

Action of Oxidizing-Agents.

We have been unable to obtain any characteristic products by the oxidation of the β-bromcrotonolactone. On boiling with concentrated nitric acid oxidation takes place, but carbonic dioxide is evolved in abundance, and no other definite products were isolated. When heated with bromine in aqueous solution the addition-product is apparently formed at first, but on boiling this is soon broken up with the evolution of carbonic dioxide. We also noticed in this case the formation of a small amount of a highly crystalline body which on recrystallization from alcohol formed long lustrous prisms. The melting-point (54°), the camphor-like odor, and other physical properties, render it extremely probable that this substance was pentabromethane, but it was insufficient in quantity for analysis. The aqueous solution upon evaporation gave a small viscous residue, from which on long standing a few microscopic rhombic plates separated which appeared to be mucobromic acid.

[*To be continued.*]

AN ISOTHERMAL CURVE OF SOLUBILITY OF MERCURIC AND SODIUM CHLORIDES IN ACETIC ETHER.

By C. E. Linebarger.

At the conclusion of a paper "On the Existence of Double Salts in Solution,"[1] it was stated that the author's intention was to make a study of all the states of equilibrium of the system: corrosive sublimate, common salt, acetic ether. It is found to be impossible, however, to complete the investigation. The results that have already been obtained are here given.

The first point to be determined was the solubility of each of the salts in the ether. Sodium chloride was found to be but slightly soluble: 100 molecules of the liquid dissolving 0.031 molecule of the salt at 17°, and 0.037 molecule at 40°. Its solubility being so slight may be neglected. The solubility of mercuric chloride is given in Table I.

TABLE I.

Solubility of Mercuric Chloride in Acetic Ether.

Temperatures	0°	13°	30°	40.5°	50.2°
Molecules $HgCl_2$ to 100 mols. $C_4H_8O_2$	15.4	15.9	16.0	16.1	16.3

As the table shows, the solubility varies but slightly with the temperature. All of the subsequent experiments were carried out at about 40° C.; the temperature did not vary more than 0.05° during an experiment.

At 40°, 100 molecules of acetic ether dissolve 16.0 molecules of mercuric chloride, or 0.037 molecule of common salt. If to the saturated solution of the first salt, sufficient quantities of the second be added, it enters into solution, and the resultant solution is able to dissolve still more of the first salt. The ether in contact with an excess of each of the salts forms a solution in which are 40 molecules of corrosive sublimate and 20 molecules of sodium chloride to 100 molecules of the solvent. In general,

[1] This Journal 15, 337.

when a solution of mercuric chloride in acetic ether of any concentration possible is brought into contact with an excess of sodium chloride, a solution results in which twice as many molecules of the former salt are present as molecules of the latter, that is, the double salt $(HgCl_2)_2.NaCl$ is formed. But what will be the composition of the solution if there be a deficiency of sodium chloride? To get an answer to this question, the following series of experiments were performed: A solution saturated with both the salts was put in a flask set in a thermostat, and a little more acetic ether, together with a large excess of corrosive sublimate, was added. This was frequently shaken for about 12 hours, and then a sample of the clear solution was drawn off and analyzed. More ether was added to the contents of the flask, care being taken that a large excess of mercuric chloride was always present. In this way, solutions saturated with mercuric chloride, but containing less and less sodium chloride, were obtained. As a "control," several solutions were prepared with weighed quantities of the constituents. The results obtained with them were entirely concordant with those obtained by the other method. The compositions of the solutions analyzed are given in Table II.

TABLE II.

Solubility of Sodium Chloride in Solutions of Mercuric Chloride in Acetic Ether.

100 molecules acetic ether dissolve:

Mols. $HgCl_2$.	Mols. NaCl.	Mols. $HgCl_2$.	Mols. NaCl.
40.0	20.0	18.0	5.1
38.1	19.6	16.4	4.3
36.0	19.2	14.1	3.8
34.9	18.5	13.2	2.9
34.8	18.3	12.4	2.3
32.1	13.8	12.0	1.6
28.0	9.1	12.2	1.3
22.8	7.0	12.9	0.8
22.9	7.0		

The results are shown graphically in Fig. 1, where the axis of abscissæ represents the number of molecules of mercuric chloride, and that of ordinates the number of molecules of sodium chloride to 100 molecules of acetic ether.

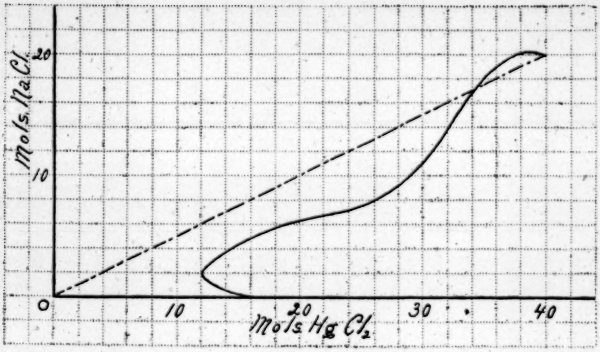


FIG. 1.

An inspection of the curve shows that the addition of a little sodium chloride diminishes the solubility of mercuric chloride. The maximum of diminution is reached when two molecules of common salt have gone into solution. The solubility of both the salts then increases at first slowly, then more rapidly. The remarkable thing about the curve is that for the values of the abscissæ between 12 and 16, there are two values of the ordinates, or, in other words, two saturated solutions of common salt in corrosive sublimate solutions are possible for a certain range of concentrations.

THE BENZOYL HALOGEN AMIDES.

BY C. E. LINEBARGER.

The halogen amides of acid radicles have been studied principally by Hofmann,[1] Bender,[2] and Hoogewerff and van Dorp.[3] In these compounds the proximity of the nitrogen and halogen

[1] Ber. d. chem. Ges. **14**, 2725; **15**, 407, 752, 977. [2] *Ibid.* **19**, 2272.
[3] Recueil trav. chim. **6**, 373; **8**, 173; **9**, 33; **10**, 4.

atoms, the latter of which are generally so capable of reaction, seems to indicate that certain important syntheses may be effected by their aid. Bender[1] has sought, indeed, to substitute certain groups of atoms in the place of the chlorine atom in benzoyl chloramide, but his efforts were not successful. Thinking that perhaps the bromine atom of benzoyl bromamide would prove more tractable, the author has performed certain experiments upon that compound. The experiments did not, however, give the desired result, benzamide being the only crystallizable compound obtained. Although the results in general were negative, still in the course of the work facts were obtained in regard to the preparation and properties of the halogen amides which it may be well to make known.

I. *Benzoyl bromamide.*—After a number of experiments upon the preparation of this substance, that which gave the best results was found to be the following: One molecule (80 grams) bromine is added to one molecule (60 grams) finely powdered benzamide contained in a large flask set in cold water. The amounts given in parentheses are convenient working-quantities, but it seems to make no difference in the yield if other quantities be taken. But little heat is evolved on the addition of the bromine. The reddish-brown mass that results must be well stirred together with a glass rod, in order that no benzamide may remain unattacked by the halogen. A solution of a little more than one molecule (30 grams) of caustic potash in 700–800 grams water is now added in small portions, the flask being well shaken after each addition and care being taken that no rise of temperature ensues. The resultant yellowish solution is filtered by the aid of a suction-pump from the solid product, and the latter is washed free from alkali with small quantities of water. The compound is slightly soluble in alkaline solutions, for on dilution of the first filtrate by the wash-water, a small quantity of a light flaky precipitate separates out. This is filtered off, washed and added to the main portion of product. The united masses are dried thoroughly by pression between folds of filter-paper, and dissolved in boiling benzene, from which on cooling it crystallizes in small plates. About 90 per cent. of the theoretical yield is thus obtained. A determination of the nitrogen gave 7.14 per cent., instead of the theoretical 7.00 per cent. Benzoyl bromamide melts at 171°, with slight decomposition. It is soluble in alcohol, and in ether and alcohol, crystallizing best from the latter solvent.

[1] *Loc. cit.*

II. *Benzoyl chloramide.*—As stated above, this compound has already been prepared by Bender. His method consisted in the action of chloride of lime in concentrated aqueous solution on benzamide dissolved in water acidified with acetic acid. It may also be easily obtained by the action of hydrochloric acid on benzoyl bromamide. When the strong acid is added to the bromamide contained in an evaporating-dish, the mass turns at first yellow and then red, from separation of bromine, which is expelled by heating on a water-bath. The residue is filtered and washed free from acid with water. It is then dissolved in boiling water and the solution concentrated until, on cooling, a crop of fine soft crystals separates out. By concentration of the mother-liquor, new crops may be obtained. The bromamide can in this way be almost quantitatively converted into the chloramide.

Benzoyl chloramide melts at 113°, is but slightly soluble in cold water, more so in boiling water; it is almost insoluble in alcohol or benzene even at their boiling-points.

III. *Benzoyl iodoamide* cannot be obtained by the application of the methods employed in the preparation of the brom- and chloramides. Only benzamide is obtained when iodine and benzamide are melted in a closed vessel and the resultant product treated with caustic-potash solution. It is doubtful whether the substance is capable of existence.

PENTOSANS IN PLANTS.[1]

By G. de Chalmot.

I.—*Notes concerning the Quantitative Estimation of Pentosans.*

I have used throughout with a slight alteration the method originally advised by Tollens and myself and somewhat modified by Flint.[2] Since this method was never fully published in an American journal, I shall describe it in brief here.

5 grams of the material to be analyzed are distilled with hydrochloric acid (of 12-per cent. HCl), with constant renewal of that

[1] This Journal **15**, 21, 276; J. Am. Chem. Soc. **15**, 618. [2] Landw. Vers. Stat. **43**, 398.

lost by distillation, until the distillate no longer shows the furfurol-reaction with aniline acetate. The distillation should be so regulated that 30 cc. of distillate are obtained in 10 to 15 minutes. The total volume of the distillate is measured, and after neutralizing with bicarbonate of sodium and slightly acidifying with acetic acid, enough sodium chloride is added for the liquid to contain about 16.3 per cent. of sodium chloride after its volume has been brought to 500 cc. by adding distilled water. A table in the original paper of Flint mentions the quantities of sodium chloride to be added to a certain volume of distillate. This addition of sodium chloride is made in order to bring the solution to a standard strength, and is necessary, since furfurol phenylhydrazone is less soluble when the sodium chloride solution is stronger.

Phenylhydracine acetate is now added in order to precipitate the furfurol in the form of hydrazone.[1] The liquid is stirred for half an hour and filtered, and the hydrazone washed with about 100 cc. of distilled water. For filtering the same tubes are used as in Allihn's gravimetric method for determining glucose, the filter being of glass-wool. For drying the hydrazone the tubes are heated in an air-bath to 50°–60° C. and are connected with an air-pump. The air is exhausted, and a slow current of dried air is passed through. The hydrazone will dry in 1½ to 3 hours, according to the power of the pump. After weighing the tubes, the hydrazone is dissolved in warm alcohol and the tubes are weighed again. The difference between the weighings indicates the amount of hydrazone.

The amount of furfurol phenylhydrazone ($C_{11}H_{10}N_2O = 170$) multiplied by $\frac{96}{170}$ or 0.516, indicates the amount of furfurol ($C_5H_4O_2 = 96$) found. Since, however, a small amount of furfurol phenylhydrazone is soluble in the sodium-chloride solution, Tollens and Flint multiply by 0.538.[2] Empiric formulæ are used for calculating the percentages of pentoses (or of pentosans) in the original substances.

My slight modification of this method is, that instead of measuring the distillate and adding to it a calculated amount of sodium chloride, I at once bring the volume of the neutralized liquid to 500 cc. by adding a 19.3-per cent. sodium-chloride solution

[1] I usually add 20 cc. of a solution containing 5 per cent. of phenylhydracine hydrochloride and 5 per cent. of sodium acetate.

[2] This figure is in most instances too high.

(19.3-per cent. NaCl = 12-per cent. HCl). I neglect the small amount of furfurol phenylhydrazone that is soluble in this solution, I further assume that pentosans yield 50 per cent. of furfurol. These pentosans may then be xylan, araban, riban [1] (adonan ?) or others. I am warranted in doing so, for I do not care to obtain absolute figures, but only the relation between the amounts of pentosan in similar vegetable matters. For example, I compare the one wood with the other, but seldom wood with leaves or seeds.

I no longer use the method of slow distillation[2] even for seeds, for the results obtained by it are perceptibly lower than those obtained by a quick distillation. A thoroughly mixed and very finely pulverized sample of oak leaves yielded by slow distillation 3.67 per cent. of furfurol = 7.34 per cent. of pentosan, as the average of 8 analyses. The same sample yielded by quick distillation 4.57 per cent. of furfurol = 9.14 per cent. of pentosan as the average of 4 analyses.

Where great accuracy is necessary, I make the analyses of the substances to be compared, side by side. In this manner I was able to prove that pentosans are not formed by the assimilation-process.[3]

In the cases where the analyses have been made side by side, I have marked them both with x or with xx.

As by distillation of vegetable matter with hydrochloric acid not only furfurol, but also methyl furfurol and other aldehydes are produced, the insoluble hydrazone obtained by adding phenylhydracine to the distillates is not pure furfurol phenylhydrazone. In the instance of some hard woods the hydrazone contains less impurities than where oak leaves or seeds have been used. If the hydrazone contains more impurities, its melting-point is lower, and it decomposes more readily, for which reason the results obtained by the analyses become less constant, unless great care is observed. I experienced this especially when estimating pentosan in corn seed. The hydrazone that I obtained could stand at the utmost a temperature of 55° C. It was therefore especially necessary completely to exhaust the air in the tubes in order to dry the hydrazone quickly.

Since the composition of the hydrazone varies according to the

[1] E. Fischer: Ber. d. chem. Ges. **26**, 633.
[2] This Journal **15**, 276.
[3] J. Am. Chem. Soc. *l. c.*

material from which it is derived, its estimation does not give an absolute measure of the quantities of pentosan in the material. But since the larger part of those hydrazones that can stand heating at 55° C. consists of furfurol hydrazone, we can safely use the gravimetric method for comparing the amounts of pentosan in similar material.

II.—*The Changes in the Percentage of Pentosan during the Growth of the Organs of the Plant.*

In a former investigation[1] I have found that the percentage of pentosan in clover hay increases from 9.2 per cent. at the beginning of the flowering to 10.5 per cent. at the end of this period. Stone obtained similar results.[2] He found that the pentosans in *Phleum pratense* increased from 15.65 to 16.17 per cent., and in another case from 12.59 to 14.26. Since, however, these results were not obtained with a view to the subject now under discussion, I have investigated it anew and now communicate the results obtained.

Experiment 1.—Young corn plants, of which the tassels were still in the earliest stages of development, were investigated. Samples were made of:

I. The tops of the stems, including the youngest undeveloped leaves and the undeveloped tassels.

II. Full-grown parts of leaves picked at 1 p. m.[3]

III. The lowest two internodes of the stem without sheaths of leaves.

	I.	II.	III.
Percentage of pentosan[4]	5.23	16.64	12.65

Experiment 2.—Red-oak leaves picked from the same shrubs at 1 p. m. of the same day contained:

	Percentage of Pentosan.
Young leaves	5.29
Fully developed leaves	9.77

In both instances the full-grown organs of the plants contained much more pentosan than the organs still in development.

I now investigated whether the percentage of pentosan increases in full-grown organs.

[1] Author's Inaug. Diss., p. 33.

[2] Agric. Sci. **7**, 9.

[3] Leaves contain more pentosan in the morning than later on in the day. *Vide* J. Am. Chem. Soc. **15**, 618.

[4] The percentages given are relative to dry matter.

Experiment 3.—Full-grown white-oak leaves contained on the morning of July 7, 7.16 per cent. of pentosan.

Leaves of the same shrubs and branches contained in the middle of October, when they were still perfectly sound and healthy, 9.36 per cent. of pentosan.

Experiment 4.—Full-grown white-oak leaves contained on the morning of July 13, 8.30 per cent. of pentosan.

Perfectly healthy leaves of the same shrubs contained in the middle of October, 10.30x per cent. of pentosan.

Leaves of which the color had turned into red, picked at the same time as the former, and from the same shrubs, contained 11.30x per cent. of pentosan.

The pentosan in the living oak leaves therefore still increases after they are full-grown. In Experiment 4 we see that also after the death of the leaves the percentage of pentosan increases. This can be due to one or more of the following reasons:

1. A decomposition or washing-out of other substances (not pentosan) of the leaves.

2. A removal of other substances out of the leaves into the stems.

3. A formation of pentosan out of other substances after death.

If the second reason was the only one, a rapid removal of substances out of the leaves would probably take place during the last days before death, for the green and living leaves, picked at the same time as the red leaves, died soon afterwards. Such a quick removal seems to be contradicted by the following result, not obtained, however, with oak leaves.

Experiment 5.—Leaves of *Maclura aurantiaca* picked on October 22, perfectly green and sound, contained 8.04x per cent. of pentosan.

Leaves off the same limb alternating with the former were picked on October 29, when the green color was fading in several spots, 8.09x per cent. of pentosan.

The excess of pentosan in dead leaves is therefore most likely not alone due to a removal of other substances.

That pentosans are formed after death seems most improbable, on taking into account the results obtained with woods, reported farther below. I therefore take for granted that the pentosans in the leaves are less subject to putrefaction and leaching out than other leaf-substances, and besides are not removed to any extent

out of the leaves before death. In leaves that decompose more quickly than oak leaves—for example, corn leaves—the difference is more apparent.

Experiment 6.—Green and healthy corn leaves picked at 6 p. m., 14.5 per cent of pentosan.

Dead leaves of the same plants picked at the same time, 24.6 per cent. of pentosan.

In other organs than leaves I also found the percentage of pentosan to increase with age, as, for example, in corn-cobs and oak wood.

Experiment 7.—Axil part of corn-cobs of which the seeds were in the earliest stages of development, 29.3 per cent. of pentosan.

Axil part of corn-cobs of which the seeds were ripe, picked from the same lot of plants as the former, 33.3 per cent. of pentosan.

Experiment 8.—Wood of *Quercus nigra* of 1 to 2 years old, including unfinished young wood, collected in the beginning of August from a standing tree, 17.3x per cent. of pentosan.

Wood of 10 and more years old, collected at the same time off the same tree, 20.3x per cent. of pentosan.

According to Experiment 8, the youngest unfinished wood contains less pentosan than when its formation is accomplished. Wieler[1] found in young wood of *Pinus sylvestris* 15.24 and 14.05 per cent. of wood-gum. Since pine wood does not contain more than 10 per cent. of pentosan, Wieler's result seems to indicate that the young unfinished wood of this tree contains more pentosan than the wood of which the formation is accomplished. This would contradict my result above. It is, however, probable that wood-gum from pine wood contains much mannan, since Tollens and Lindsay[2] found mannose in an extract of pine wood which had been obtained with sodium bisulphite in the paper factories. I shall investigate this subject next summer.

III.—*Examination of Woods.*

Since wood is one of the vegetable matters most rich in pentosan, the study of different woods promised to reveal some facts as to the physiological significance of the pentosans. In the following list I have given the percentages of pentosan which I found in wood of different trees:

[1] Landw. Vers. Stat. **32**, 307. [2] Ann. Chem. (Liebig) **267**, 341.

Species.	Family.	Origin.	Per cent. of Pentosan.
Liriodendron tulipifera	*Magnoliaceæ*	Virginia collection[1]	19.1
Magnolia acuminata	*Magnoliaceæ*	See Exp. 11	17.7
Prunus Pennsylvanica	*Rosaceæ*	Virginia collection	19.7
Cercis Canadense	*Leguminosæ*	See Exp. 18	21.1
Acer dasycarpum	*Sapindaceæ*	Virginia collection	22.1
Liquidambar Styraciflua	*Hamamelideæ*	Virginia collection	21.1
Ilex opaca	*Ilicineæ*	Virginia collection	24.6
Ampelopsis quinquefolia	*Vitaceæ*	Virginia collection	20.9
Cornus florida	*Cornaceæ*	Virginia collection	21.6
Nyssa sylvatica	*Cornaceæ*	Virginia collection	20.8
Fraxinus Americana	*Oleaceæ*	Virginia collection	17.5
Fraxinus platicarpa	*Oleaceæ*	See Exp. 16	17.4
Juglans cinerea	*Juglandaceæ*	Virginia collection	19.2
Carya alba	*Juglandaceæ*	Virginia collection	21.2
Salix spec.	*Salicineæ*	Virginia collection	21.0
Betula spec.	*Cupuliferæ*	Virginia collection	23.4
Fagus ferruginea	*Cupuliferæ*	Virginia collection	21.0
Quercus Phellos	*Cupuliferæ*	Virginia collection	21.6
Quercus alba	*Cupuliferæ*	Virginia collection	20.4
Quercus rubra	*Cupuliferæ*	Virginia collection	21.7
Quercus nigra	*Cupuliferæ*	Virginia collection	21.3
Ulmus Americana	*Urticaceæ*	Virginia collection	17.4
Platanus occidentalis	*Platanæ*	Virginia collection	21.6
Juniperus Virginiana	*Coniferæ*	Virginia collection	10.4
Pinus strobus	*Coniferæ*	White pine timber	7.5
Pinus mitis	*Coniferæ*	Yellow pine timber	8.8
Tsuga Canadensis	*Coniferæ*	20-year old Christmas-tree	6.0

Out of these figures I have not been able to trace any relation between the percentage of pentosan in wood and its hardness, durability, toughness or other qualities,—which of course does not imply that such relations cannot exist. The only regularity observed is that wood of *Coniferæ* contains much less pentosan than that of *Dicotyledoneæ*. The former contains only 10 per cent., or less, of pentosan; the latter from 17 per cent. to 25 per cent. Analyses which I made some years ago of German woods[2] confirm this conclusion. I found:

	Furfurol.	Pentosan.
Fagus sylvatica	12.6	25.2 per cent.
Picea excelsa	5.0	10.0 "

[1] "Virginia collection" means a collection of Virginia woods in blocks exhibited in New Orleans in 1885, samples of which were kindly put at my disposition by Colonel Whitehead, Commissioner of Agriculture in Virginia. [2] Author's Inaug. Diss. p. 39.

These figures cannot be directly compared with the former, for they have been obtained by a somewhat different method.

It was of consequence to know whether the amount of pentosan increases in wood after this is ready made. In order to investigate this I made use of discs of wood also belonging to the collection already mentioned. I have collected wood of different ages from the same discs by drilling holes in it with a brace and bit. The holes had a diameter of 1 cm.

Experiment 9.—With *Quercus nigra.*

I. Wood of 2–12 years, 21.1 per cent. of pentosan.
II. Wood of 69 years, 21.0 per cent. of pentosan.
III. Wood of 109–110 years, 20.6 per. cent. of pentosan.

Experiment 10.—With *Liriodendron tulipifera.*

I. Wood of 19–21 years, 19.6 per cent. of pentosan.
II. Wood of 59–60 years, 18.8 per cent. of pentosan.

Experiment 11.—With *Magnolia acuminata.*

The year-rings of this tree were not distinctly discernible.

I. Wood younger than 10 years, 17.7x per cent. of pentosan.
II. Old heart-wood, 16.8x per cent. of pentosan.

Experiment 12.—With *Platanus occidentalis.*

I. Wood of 4–10 years, 19.6x per cent. of pentosan.
II. Heart-wood of 71–79 years, 19.4x per cent. of pentosan.

Experiment 13.—With *Prunus Pennsylvanica.*

I. Wood of 4–12 years, 21.5x per cent. of pentosan.
II. Wood of 4–12 years, 20.8xx per cent. of pentosan.
III. Heart-wood of 60–70 years, 19.5x per cent of pentosan.
IV. Heart-wood of 60–70 years, 19.2xx per cent. of pentosan.

I and II and also III and IV represent wood specimens originating from different borings on the same cross-section of one disc.

In these experiments the older wood always contained less pentosan than the younger. The difference is the greatest in *Prunus Pennsylvanica*, where it amounted to about 2 per cent.

The analyses of the wood of this tree moreover show that the percentage of pentosan is not exactly the same in different portions of wood of the same age and situated on the same cross-section. In other woods the older portions contain more pentosan than the younger, as the following results show:

Experiment 14.—With *Juglans cinerea.*

I. Wood of 4–18 years, 18.1x per cent. of pentosan.
II. Wood of 4–18 years, 17.9 per cent. of pentosan.
III. Heart-wood of 60–65 years, 19.2x per cent. of pentosan.
IV. Heart-wood of 60–65 years, 18.9 per cent. of pentosan.

I and II and also III and IV are of different borings on the same cross-section of the same tree.

Experiment 15.—With *Fraxinus Americanus.*

I. Wood of 2–7 years, 17.9x per cent. of pentosan.
II. Heart-wood of 51–52 years, 18.8x per cent. of pentosan.

In connection with these experiments I also ascertained whether the amount of pentosan in woods changes materially when a stronger decomposition than that into heart-wood takes place. I had 3 discs at my disposition which contained spots where the wood was dry-rotten.

Experiment 16.—With *Fraxinus platicarpa.*

I. Heart-wood, 17.4x per cent. of pentosan.
II. Dry-rotten wood about 5 years older, 16.2x per cent. pentosan.

Experiment 17.—With *Prunus Pennsylvanica.*

I. Heart-wood, 19.8x per cent of pentosan.
II. Dry-rotten wood of about the same age, 19.9x per cent. of pentosan.

The specimens were of the same disc of wood as those in Experiment 13, but of the other cross-section.

Experiment 18.—With *Cercis Canadense.*

I. Heart-wood, 21.1x per cent. of pentosan.
II. Dry-rotten, 21.9x per cent. of pentosan.

Experiment 19.—With *a fence board of pine wood.*

I. Sound wood, 10.2x per cent. of pentosan.
II. Rotten wood, 7.9x per cent. of pentosan.

We perceive no regularity in these results, and I therefore conclude that the increase or decrease in the percentage of pentosan in ready-formed wood depends upon the individuality of the tree (or its species) to which it belongs. In one tree the pentosan therefore decomposes more easily than the other substances in the wood; in another the reverse takes place. Perhaps also an infiltration of wood-gum into heart-wood, as Hartig claims,[1] takes place in some woods (Juglans). I believe it further to be safe to conclude that at least in the majority of cases, and most probably in all instances, a formation of pentosan does not take place after the wood ts ready made.

Theoretical Conclusions.

I have proved that pentosans are not formed by the assimilation process. They are therefore formed, directly or indirectly, out of hexoses. How and where does this take place?

Crosse, Bevan and Beadle[2] have made a step towards solving the first part of this question. They found that if starch, cane-sugar, sugar of milk, or cotton-cellulose—in one word, if hexosans are gradually oxidized with chromic acid and afterwards distilled with acids, large amounts of furfurol are obtained. By this oxidation of hexosans, substances are therefore formed that yield furfurol by hydrolysis. Whether these substances are pentosans is not as yet certain. It could as well be glucuronic acid or its isomeres, which also yield much furfurol by hydrolysis. Further communications on this point have been promised. However this may be, the formation of pentosan in plants is most probably bound up with the action of the living cell. After death pentosan is no longer formed; the analyses of woods seem to indicate this clearly. In wood that is especially rich in pentosan the amount of these substances, as we just concluded, does not increase after its development is complete.

The place where pentosans are formed may be the cell wall. Wood, dead corn leaves, straw and other materials where the contents of the cells have much diminished, and which therefore

[1] Botan. Centralbl. **56**, 357.
[2] Ber. d. chem. Ges. **26**, 2503.

are rich in cell walls, contain also much pentosan. In many instances the pentosan seems, moreover, to be united with cellulose, since it cannot easily be separated from it.[1] Since, however, the presence of pentosan cannot be ascertained microscopically, the places where it is found in the living plant are only in a few instances known with absolute certainty.

Schulze's paragalactan, which yields by hydrolysis arabinose, besides galactose,[2] was found by Prof. Kramer[3] to be contained in the walls of the cotyledonar cells of *Lupinus luteus*. Amyloid, which occurs in the cell walls of many plants, contains, according to Winterstein,[4] more than 30 per cent. of pentosan. It is this matter that acts as a reserve substance in the seeds of *Tropæolum majus*.

Concerning the physiological significance of the pentosans in plants I might at present suggest the following:

Pentosans accumulate during the whole life of the organs; the plant seems to be profuse with pentosans. We have, however, no reason to believe that the pentosans are waste-products. They are transported to a limited extent, since we find small amounts of soluble pentosans in all plants. Pentosans are also resolved in the seeds and transported into the young plants, though not as readily as the hexosans (as starch).

In seeds of *Propæolum* the significance of the pentosans has been proven, since they conduct themselves therein entirely as reserve substances.

It is probable that the pentosans have some importance for the formation of wood, since we find them especially in organs that have turned into wood. Large amounts of pentosan are, however, not essential for the wood-formation, since we find in some pine woods (hemlock) only 6 per cent. These investigations are to be continued.

[1] See E. Schulze: Ber. d. chem. Ges. **23**, 2579, 3330; **24**, 2277. Ztschr. physiol. Chem. **16**, 387. Author's Inaug. Dis., p. 40. Winterstein: Ztschr. physiol. Chem. **17**, 381. Tollens and Schulze: Ann. Chem. (Liebig) **271**, 55. W. Hoffmeister: Landw. Vers. Stat. **39**, 466. Crosse and Bevan: J. Chem. Soc., 1889, p. 199.

[2] Landw. Vers. Stat. **41**, 223.

[3] *Ibid.* **36**, 454.

[4] Ber. d. chem. Ges. **25**, 1237, where also the literature about this substance is referred to.

NOTE ON PENTOSANS IN SOILS.

By G. de Chalmot.

There are pentosans which resist putrefaction, and for this reason we find pentosans in soils. This was already stated some years ago by a French investigator.[1] In the case of three soils I have estimated the percentage contents of pentosan and of humus, and therefore the ratio which the former bears to the latter. The soils were sifted through a 1-mm. sieve. 25 or 50 grams were taken for analysis.

Description of Soil.	Humus.	Pentosan.	100 parts of Humus contain . . . parts of Pentosan.
Wood soil	23.42 per cent.	0.75 per cent.	3.2
Garden soil	9.85	0.39	4.0
Poor sandy soil	2.68	0.04	1.5

Richmond, Va., *February*, 1894.

Contribution from the Chemical Laboratory of Lehigh University.

ON PHOSPHO-HYDROCYANIC ACID.

By W. B. Shober and F. W. Spanutius.

Preliminary Paper.

One of us, several years ago, working under the direction of Dr. Launcelot Andrews, attempted to prepare the phosphorus analogue of hydrocyanic acid—an acid the composition of which would be represented by the formula HCP—by heating chloroform and zinc phosphide together in a sealed tube. The reaction was expected to take place in this way:

$$2CHCl_3 + Zn_3P_2 = 2HCP + 3ZnCl_2.$$

The results obtained were not satisfactory. Recently the work

[1] I have been unable to trace the paper alluded to, and I therefore cannot communicate where it was published.

has been taken up again, in this laboratory Other methods have been tried and we have succeeded in preparing the sodium salt of phospho-hydrocyanic acid.

When dry ammonia is passed over heated sodium the reaction expressed by the following equation takes place:

$$2Na + 2NH_3 = 2NH_2Na + H_2.$$[1]

When sodium amide is treated with carbon monoxide, under the proper conditions, sodium cyanide is formed:

$$NH_2Na + CO = NaCN + H_2O.$$

We repeated these experiments, substituting phosphine for ammonia, when the following reactions took place:

$$2Na + 2PH_3 = 2PH_2Na^2 + H_2;\ \text{or, possibly,}$$
$$2Na + PH_3 = Na_2HP + H_2;\ \text{or}$$
$$3Na_2 + 2PH_3 = 2Na_3P + 3H_2.\ \text{And then,}$$
$$PH_2Na + CO = NaCP + H_2O.$$

The method of procedure was as follows: A clean, thoroughly dry piece of hard-glass tubing about 75 cm. long and 1.5 cm. in diameter was placed in a combustion-furnace. To the front end was attached a calcium-chloride tube, then a Woulff bottle containing concentrated sulphuric acid, the inlet and outlet tubes reaching *almost* to the surface of the acid; finally, two Woulff bottles containing a saturated solution of copper sulphate. The object of these last was to decompose any phosphine which had escaped the action of the sodium. The last bottle was connected with a hood. To the rear end of the glass tube was attached a long (35 cm.) drying tube containing soda-lime; to this, another tube of the same length filled with small pieces of potassium hydroxide; to this two wash-bottles containing sulphuric acid, and finally a wash-bottle containing potassium-permanganate solution. Hydrogen was passed through the entire apparatus until all air was expelled.

While a rapid current of hydrogen was still passing through, a small quantity (1.5 grams) of sodium, free from oxide and

[1] Beilstein and Geuther: Ann. Chem. (Liebig) **108**, 88.

[2] It is not known certainly that $NaNH_2$ is the correct formula for the compound formed by the action of sodium upon ammonia. Assuming that $NaNH_2$ is the correct expression, the composition of the phosphorus compound formed under similar conditions is probably to be expressed by $NaPH_2$, although it may be Na_3PH or Na_3P. In any case it is probably similar in its composition to the sodium compound, which, whatever it may be, yields sodium cyanide when treated with carbon monoxide. So this compound of phosphorus, whatever its composition, yields, when treated with carbon monoxide, *sodium phosphocyanide*.

hydroxide, was transferred to the glass tube. In order to prevent the action of the air and moisture and to keep the surfaces as bright as possible, the outside coating of the metal was removed under benzene. Without removing the benzene which adhered to it, the metal was quickly placed in the tube. The benzene was expelled by the aid of heat and the rapid current of hydrogen. When the benzene was completely removed, the hydrogen generator was replaced by a phosphine generator, from which all air had previously been expelled, and the permanganate and sulphuric-acid wash-bottles removed.[1] The phosphine was obtained by treating zinc phosphide with sulphuric acid. Heat was applied to the sodium until it melted. Phosphine was then generated slowly and passed through the apparatus. The bright silvery surface of the sodium began to blacken and show evidence of some action. Small black particles floated around on the surface of the metal, until finally the whole mass became covered with a thick black crust. The phosphine was passed until all of the sodium was converted into this black substance, then, without allowing the apparatus to cool, dry carbon monoxide, free from air and carbon dioxide, was passed over this black substance for an hour. After the furnace was cool the glass tube was removed. On exposure to the air small particles of the substance ignited spontaneously. The tube was at once closed, when these small explosions ceased. It was then filled with absolute alcohol which had been standing over anhydrous copper sulphate for three months, corked up and allowed to stand for 12 hours. The alcohol became darker in color until it was a deep red. A sediment was deposited. Since the compound of sodium and phosphine is extremely unstable—decomposing upon exposure to the air—and since the difficulties in the way of establishing its composition are very great—in fact, even greater than those that are encountered when an attempt is made to determine the composition of the compound which is usually represented by the formula $NaNH_2$;—further, since sodium phosphocyanide is also extremely unstable; we have found it impossible up to the present to analyze these compounds. Nevertheless, satisfactory evidence of the composition of sodium phosphocyanide is obtained by a study of its decomposition-products.

[1] Phosphine decomposes on passing through concentrated sulphuric acid. It deposits a reddish-yellow substance, presumably phosphorus, which on standing in contact with the acid explodes violently.

The alcohol and residue were transferred to a beaker and a small quantity of water added. Phosphine was immediately evolved in large quantites. This may have been due to the decomposition of sodium phosphocyanide, monosodium phosphine, disodium phosphine, trisodium phosphine, or to several of these compounds. The black substance above referred to probably consists of a mixture of at least two of these compounds. Since sodium cyanide is decomposed by alkalies into formic acid and ammonia, sodium phosphocyanide should be decomposed into formic acid and phosphine. The possible reactions giving rise to phosphine are these:

$$NaH_2P + H_2O = NaOH + PH_3.$$
$$Na_2HP + 2H_2O = 2NaOH + PH_3.$$
$$Na_3P + 3H_2O = 3NaOH + PH_3.$$
$$NaCP + H_2O = H.CO.ONa + PH_3.$$

Each of these compounds would yield phosphine, but there is only one that could yield formic acid.

Water was added until phosphine ceased to be evolved. The solution was then evaporated, a fluffy black substance was formed and filtered off. Upon drying it, the quantity obtained was too small to investigate. The filtrate, which was strongly alkaline, was neutralized with phosphoric acid and subjected to distillation. A portion of the distillate was heated to 60°–70° and a solution of mercuric chloride was added. A heavy precipitate of mercurous chloride gave unmistakable evidence of the presence of formic acid. The presence of formic acid shows conclusively that the reaction referred to above had taken place, thus showing that the sodium salt of phosphohydrocyanic acid is capable of existence.

With the advent of this compound a new field is opened. If a class of phosphorus compounds analogous to the cyanides, both organic and inorganic, can be prepared, they will form a remarkable series of compounds, each one of which will be an additional link in the chain of analogy between the related elements, nitrogen and phosphorus.

This also foreshadows the existence of a compound the composition of which will probably be represented by CP or C_2P_2, analogous to cyanogen.

We have been obliged to discontinue this investigation for the present, but in the near future we shall take it up again.

South Bethlehem, Pa., *February*, 1894.

REVIEW.

TABELLARISCHE UEBERSICHT DER NAPHTALINDERIVATE. Auf Grundlage des Werkes: Sur la Constitution de la Naphtaline et de ses Dérivés, par F. Reverdin et E. Noelting, unter Berücksichtigung der neueren Literatur, bearbeitet von F. REVERDIN und H. FULDA. Basel, Genf, Lyon. Verlag von Georg & Co. 1894. (Erster Theil: Tabellen. Zweiter Theil: Literatur.)

The authors of this work have attempted to give references to all articles treating of naphthalene derivatives, and to arrange these derivatives in tables in such a manner as to tell the story of their constitution in as few words as possible. The number of compounds included in the tables is 911, and these are all derivatives of naphthalene. Many of these compounds are of scientific interest, and many are now used in the dye-stuff industry, and in view of the extent of the literature it is, of course, desirable to have such an excellent work as this at hand as a guide to the sources. The earlier works upon which the present one is based are "Ueber die Constitution des Naphthalins und seiner Derivate," which appeared in 1880; and "Sur la constitution de la naphtaline et de ses dérivés," which appeared in 1888. These have brilliantly withstood the test of use, so that it is fair to assume that the new edition will maintain the high standard of its predecessors. The manuscript was finished August 1, 1893, and articles which have appeared since this date have not received consideration.

The authors do not claim thoroughness except for their references to German and French literature. They say: "Was die Literatur anderer Länder betrifft, so standen uns zwar nur die wichtigeren Zeitschriften zu Gebote, wir haben jedoch derselben noch ausserdem Rechnung getragen, soweit uns die Abhandlungen im Original oder durch Referate in deutschen oder französischen Zeitschriften zugänglich waren." While probably no great harm has resulted from this off-hand treatment of the "Literatur anderer Länder," it seems to one who has the misfortune to belong to "another country" that, in a work of this kind, we have a right to expect as thorough a consideration of the "Literatur anderer Länder" as that which is accorded to the French and German.

I. R.

NOTE.

On a new Class of Organic Bases, containing Iodine but no Nitrogen.

Victor Meyer and C. Hartmann[1] have just described some remarkable compounds containing iodine. The principal one

[1] Ber. d. chem. Ges. **27**, 426.

thus far obtained is made by treating iodosobenzene, $C_6H_5.IO$, with concentrated sulphuric acid at a low temperature. On diluting the solution thus obtained, and adding potassium iodide, a precipitate is formed which is the hydriodide of a base. The salts of the base resemble those of lead and of silver, but still more those of thallium. The sulphate is easily soluble in water, the nitrate more difficultly soluble. The iodide is a yellowish, insoluble precipitate; the bromide a pale yellowish, and the chloride a white precipitate. The aqueous solution of the free base has a *strong alkaline reaction.* It is obtained by shaking the solution of the hydriodide with silver oxide. The hydriodide, or iodide, was analyzed and shown to have the composition represented by the formula $C_{12}H_9I_3$. When subjected to dry distillation, this breaks down into monoiodo- and diiodobenzene thus:

$$C_{12}H_9I_3 = C_6H_5I + C_6H_4I_2.$$

The salts studied, in addition to the iodide, are the bromide, $C_{12}H_9I_2Br$; the chloride, $C_{12}H_9I_2Cl$; the nitrate, $C_{12}H_9I_2.NO_3$; and the sulphate, which was not analyzed.

The formation of the base is probably represented thus:

1. $C_6H_5IO + H_2O = C_6H_5I{<}^{OH}_{OH}$;

2. $C_6H_5I{<}^{OH}_{OH} + HC_6H_4IO = {}^{C_6H_5}_{IC_6H_4}{>}I.OH + H_2O + O.$

According to this, the base has the constitution expressed by the formula, $I{-}C_6H_4I{<}^{C_6H_5}_{OH}$, and it appears to be a derivative of the compound, $I{-}H{<}^{H}_{OH}$, which, as far as the composition is concerned, is analogous to hydroxylamine, $N{-}H{<}^{H}_{OH}$. But the two must differ fundamentally in their conduct towards acids. While hydroxylamine forms salts in the same way that ammonia does, by direct addition to acids, the iodo-base reacts with acids like the ammonium bases with elimination of water:

$$I{-}C_6H_4I{<}^{C_6H_5}_{OH} + HI = I{-}C_6H_4I{<}^{C_6H_5}_{I} + H_2O.$$

The authors have further obtained the compound, $I{-}C_6H_5{<}^{C_6H_5}_{OH}$, and are now engaged in studying these interesting products.

I. R.